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CONFERENCE PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE NO.2

Constellation Hotel Toronto Ontario

November 24, 1981



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The Honourable
Keith C. Norton, Q.C.,
Minister

Gérard J. M. Raymond
Deputy Minister

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INTRODUCTION

Ministry of the Environment
Province of Ontario

Technology Transfer Conference No. 2
Tuesday, November 24, 1981

Constellation Hotel
900 Dixon Road
Rexdale, Toronto
Ontario M9W 1J7

Featuring Completed Research Projects
Supported by the Provincial Lottery
Trust Fund

Sponsored and Presented by the
Research Advisory Committee
Ministry of the Environment

The Research Advisory Committee, Ontario Ministry of the Environment, sponsored Technology Transfer Conference No. 2 on November 24, 1981 at the Constellation Hotel for the purpose of distributing information arising from Provincial Lottery Research Projects and from other selected M.O.E. in-house and external research projects. At this Conference, Contractors, Principal Investigators, Liaison Officers and Researchers described and discussed results of their projects giving emphasis to useful applications of the investigational work.

The attendance of approximately 275 at this one day session was divided between two parallel sessions of their choice. The program was structured for M.O.E. Staff and Researchers, Ontario and Federal Government Personnel, Consultants, Contractors, University Personnel, Industry Representatives and Media.

Twenty-one papers were given at the Conference and of these, eighteen were supported with Provincial Lottery Trust Funds.

ACKNOWLEDGEMENT

This Conference Proceedings is issued to describe environmental oriented research projects conducted by the Ontario Government, assisted by the Federal Government, Universities and the Private Sector. All initial enquiries regarding the papers given at the Conference should be made to the authors and speakers or to their affiliation.

DISCLAIMER

The contents of this Conference Proceedings have been reviewed by the Research Advisory Committee and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Ontario Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Session Chairmen at Conference No. 2

D. A. McTavish,	Southwestern Region
B. I. Boyko,	Waste Mangement Branch
P. D. Foley,	Pollution Control Branch
G. C. Ronan,	Laboratory Services Branch

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ELLIOT LAKE RADON GAS REMOVAL PROGRAM - RESEARCH IMPLEMENTATION AND RESULTS

R.S. Eaton, Atomic Energy Control Board, Box 1046, Ottawa, Canada K1P 5S9

ABSTRACT

For the past five years, the Atomic Energy Control Board acting as the operational agency for a Federal Provincial Task Force on Radioactivity has been systematically surveying and modifying housing and other buildings in the towns of Port Hope, Elliot Lake, Bancroft and Uranium City.

In the three uranium mining communities there is some contamination in the form of waste mine rock. However, the bulk of the problem has been due to natural radon and decontamination through the removal of the source is not feasible.

Technical solutions to the problem of excess radon and radon daughters in buildings have been found which depend only upon the style of application of conventional building techniques.

Four techniques can be applied:

- a) removal of the source material: This has mainly been applied where there is a unique contamination problem.
- b) ventilation of the sub soil: For those cases where the soil is relatively porous, it has been possible to divert any radon bearing gas to the atmosphere before it enters the lived-in volume.
- c) sealing of the foundation: Standard building materials applied in a novel fashion have proven to be effective in rendering old foundations radon proof. From this, building techniques have evolved that can be applied to new construction.
- d) modification of housing air circulation system: Forced circulation through an electrostatic precipitator coupled with the controlled introduction of heated make-up air.

The promotion of energy conservation through a reduction of the ventilation rate in housing may be the key to a long term solution of the problem.

ELLIOT LAKE RADON GAS RESEARCH PROGRAM -
RESEARCH, IMPLEMENTATION AND RESULTS

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Introduction

In 1975, inspectors of the Atomic Energy Control Board (AECB), the Canadian nuclear regulatory agency, undertook a detailed survey of the Town of Port Hope, Ontario, as part of a nation-wide review of past operations and disposal practices. The Board suspected possible contamination in Port Hope since it had been used in the 30's and 40's for the refining of radium and is now the site of a uranium refining facility. During this survey which included gamma and grab sample radon measurements, it was determined that radium-bearing material had been widely spread throughout the community.

With the publicity that ensued from the Port Hope discoveries, concern was expressed that contamination might also be present at the uranium mining communities in Canada: Elliot Lake and Bancroft in Ontario and Uranium City in Saskatchewan. Subsequent surveys showed that this concern was justified.

While elevated gamma levels can be found at all locations, the main concern has been the radon and radon daughter concentrations found in occupied housing.

This paper is a discussion of the radon transport mechanism and an overview of the investigational and remedial action programs at these locations with particular emphasis on Elliot Lake. The technical solutions that have been devised to deal with the contamination are based on common North American building practices which can be readily applied to new construction.

Organization

The need for cooperation at several levels of government led to the establishment in 1976 of a Federal Provincial Task Force on Radioactivity under the leadership of the AECB. The main job of the Task Force has been to effect the clean up of Port Hope and these other locations and communities with all reasonable haste. This has meant a parallel attack at the four main locations using consulting engineering firms as project managers under a central program coordination by the AECB. Our contractor at Elliot Lake was given limited additional monies for a developmental program to search for radon gas routes and to test available

building materials as barriers and the results of this work will be provided here. Two companies are now recognized as international experts in the radon-proofing of buildings.

Criteria

The primary criteria for radon daughters in houses is 0.02 working level (WL) (AECEB Information Bulletin 77-2) averaged over a year and remedial action is taken when this value is exceeded. Since there was no integrating instrumentation readily available for this measurement at the beginning of the program, nor did time permit surveys over a year before action could be started, decisions had to be based on grab sample measurements taken over a number of weeks.

Where gamma emitting waste material is encountered, primary criteria of greater than 0.05 mR/hour (0.5 μ Sv/hr) at 1 metre indoors and 0.1 mR/hr (1 μ Sv/hr) at 1 metre outdoors has been used to initiate remedial action.

The value of 0.02 WL can be derived from the 4 working level month (WLM) criterion present in our Atomic Energy Control Regulations for occupational exposure in nuclear facilities modified by assuming continuous occupancy, by adjusting for a different breathing rate relative to the mine and by allowing for the fact that we are dealing with the public at large rather than a selected group of workers. The gamma criterion of 0.05 mR/hr (0.5 μ Sv/hr) at one metre inside a house is also derived from the 500 mRem (5 mSv) annual exposure limit for the public at large found in our Regulations.

Port Hope - a contamination problem

A total of about 3,500 houses were initially investigated from which it was determined that about 450 required work (see table 1).

Of those requiring remedial work, slightly more than half exceed the gamma radiation criterion as they involved contaminated building material. The removal of this material was relatively simple and straightforward. For the remainder most exceeded the radon/radon daughter criteria because of the nearby and extensive presence of contaminated soil.

Table 1

No. of Houses:	<u>Port Hope</u>	<u>Elliot Lake</u>	<u>Bancroft</u>	<u>Uranium City</u>
Initially Surveyed	3,500	1,920	1,170	545
Requiring remedial work γ and/or $\alpha > 0.02$ WL	450	120	140	100
Proportion	13%	6%	12%	18%
Source	Contamination	Largely natural with some surface contamination		

Total number of grab samples taken is approaching 60,000.

The procedure for radon reduction was to find and remove the source. For those houses requiring detailed investigation, test borings were made outside the structure in the vicinity of the foundation and at points of high surface gamma readings. Internal boring was also undertaken to determine the contribution from the fill under the basement floor. Vertical gamma profiles were measured from which volumes of contamination could be estimated. Sub-contractors could then be hired to remove soil within a defined area and to a certain depth. On some occasions, concrete basement floors were broken up and removed to be replaced by new concrete. Landscaping was restored and small trees, walls and driveways replaced as necessary when external cleanup was undertaken.

For some properties, this form of remedy was not effective; there seemed to be a very diffused source at a depth below any construction excavation and for which no significant gamma source could be identified. A study of a series of aerial photographs to identify past surface water movement patterns suggest that some active material from storage sites uphill from the housing had been washed downhill. As excavation in these cases was found to be impractical, other techniques were applied based on experience gained in those communities where natural materials were the main source of radiation. These techniques are described in greater detail below.

The Uranium Mining Communities of Elliot Lake, Bancroft and Uranium City

Uranium City, a frontier type community in the northern part of the province of Saskatchewan, seemed, at first sight, to have been contaminated in a way similar to that found in Port Hope. A gamma survey indicated the extensive use of slightly radioactive waste mine rock throughout the community as aggregate for

road beds, driveways, paths, building walls and sub-floor fill. However, further investigation indicated that much of this gamma radiation material was shallow in depth and could not be the cause of elevated radon in some of the structures. Furthermore, direct correlation could be found between natural occurrences as recorded by earlier prospectors and high radon levels in housing that was subsequently built at these locations.

On the other hand, as a measure of the magnitude of the waste rock problem, up to eight feet of active waste mine rock was found under several high school classrooms. This required a form of mining to remove.

A problem with Uranium City has been the quality of the housing that needed remedial action. New construction is not the responsibility of the Task Force and the mining companies have agreed to fix their own houses. In addition, the mining companies have been selling their older properties in favour of new construction. As a result most of the older buildings are now in private hands and are substandard in that basements, if they exist, are often dug out after the house has been set on wooden pilings or similar base. Such a basement may have been lined with concrete block inside the main house foundation and are not load bearing. There is often, then, open soil between sub-grade wall and the outside house wall.

Elliot Lake was the second mining community examined and it too showed many of the characteristics of Port Hope. Like Uranium City, waste mine rock was found around the town in ditches and on driveways. However, the town was partly built over a band of uranium bearing quartzite. On the other hand, our house by house survey, while showing high readings in the quartzite area, also indicated high radon in the granitic area where there is no significant known uranium concentration in the bed material.

Bancroft is a geologically complex area with a large number of small radioactive showings and with an economy partly dependent on a uranium mine. There is some waste material about the town but the main contamination is the elevated radon concentration in the soil gas. Hence the remedial techniques developed for Elliot Lake have proven successful. (See Table 1 for summary)

Remedial Action

Tests in basements with high radon concentrations indicated that emanation rates from good concrete surfaces could not support the levels measured if it is assumed that all the radon was coming through the walls (unless the aggregate was exceptionally active). This is in contrast to the work of Culot et al (1976). At the same time, the collection of soil gas in bags sealed over cracks, drains and other discontinuities indicated the influx of sufficient radon to account for the levels measured.

The concept of soil gas (oxygen depleted air) as the carrying agent for radon has been the key to the solution of the radon problem; we believe that the movement of this kind of air by whatever driving force that causes it to move into a basement is the source of the buildup of radon. We have found that the sealing of cracks, other openings and the water trapping of drains and sumps penetrating basement floors stops the entry of radon. A metre of crack may be a large enough discontinuity to raise the radon daughter concentration above criterion.

The above assumes poured concrete walls and floors of at least 20 cm (8 ins.) and 10 cm (4 ins.) thickness respectively and of appropriate strength. For those houses that use concrete blocks or are built so that there are open soil areas, the cost of sealing may be prohibitive and an approach of diverting the radon present in the soil to the atmosphere before it can enter the basement has been developed. Early tests indicated that 10 cm perforated plastic pipes placed under the basement floor on 60 cm centres (2 ft.) and manifolded into plain 20 cm chimney was sufficient to keep radon concentrations below criterion. For difficult cases, a small electric fan or wind driven fan in the stack will provide adequate suction. Where the subfloor material is suitable (loose granular), a simple penetration of the floor by a chimney may be adequate. Pumping on sumps has also been successful as these are usually connected to a buried pipe system.

Recent experience has led to a fourth technique based on modified internal air circulation. Work in Uranium City has identified a number of houses where sealing was not practical, or where the costs for remedial work of another type was not justified.

As the radon daughters are ionized, they can be removed by circulating the contaminated air through a commercially available electrostatic precipitator installed in a furnace. Fresh outside air may be introduced to provide additional dilution if necessary. Some positive pressurization is also achieved this way.

As a remedial action and assuming that the house heating is based on a central air distribution system, a precipitator and a two-speed furnace fan motor are installed. House air is therefore being slowly, continuously and quietly circulated. Fresh air is introduced to the cold air return preheated electrically as necessary so as not to upset the heating balance and at a rate to ensure an adequate number of air changes to provide dilution. The house system will then respond to normal internal temperature changes.

At present, the Task Force is paying the incremental electricity costs. However, with ownership changes, such charges should be passed over to the occupant. Some maintenance is required which is an unattractive feature of this approach.

The routes of entry and examples of technical solutions are illustrated in the sketches attached. Extensive testing under accelerated aging conditions in a laboratory has identified certain proprietary materials that make excellent radon proof and reliable crack sealers.

Representative costs

Removal of contamination	\$3,000 (external only); \$10,000, when floor removed, and hand labour required.
Sealing of foundation	\$500 simple trap replacement; \$5,000 for crack sealing in finished basement.
Subfloor ventilation	\$1,000 for stack alone; \$5,000 for floor removal and perforated pipe installation.
Modified housing air circulation	\$1,500 but ongoing annual costs
Radon proof new construction	\$1,000 - \$2,000.

New Energy Conserving Construction

A study of air change rates in Elliot Lake indicate housing there is typical of that found elsewhere on the continent with a rate of about twice per hour

(2 ach). On the other hand a measurement in a third floor unoccupied apartment showed an air change rate of once every 30 hours (0.03 ach). For the conventional housing case, radon daughter concentration averages less than 0.005 WL for correctly sealed foundations. For this apartment which was constructed from concrete at all surfaces, the radon daughter concentration exceeded 0.020 WL.

This suggests, and it has since been proven, that new air tight and radon sealed construction can produce radon daughter concentrations in excess of the Task Force criterion. This in turn indicates a further remedial method that could be applied to other housing: increase the air change rate by controlled ventilation using a heat exchanger to recover lost heat.

The problems of other contaminants in energy conserving housing with concrete basements can be treated this way. Indeed indications are that solving the other pollutants problems will deal with any radon so generated.

Summary

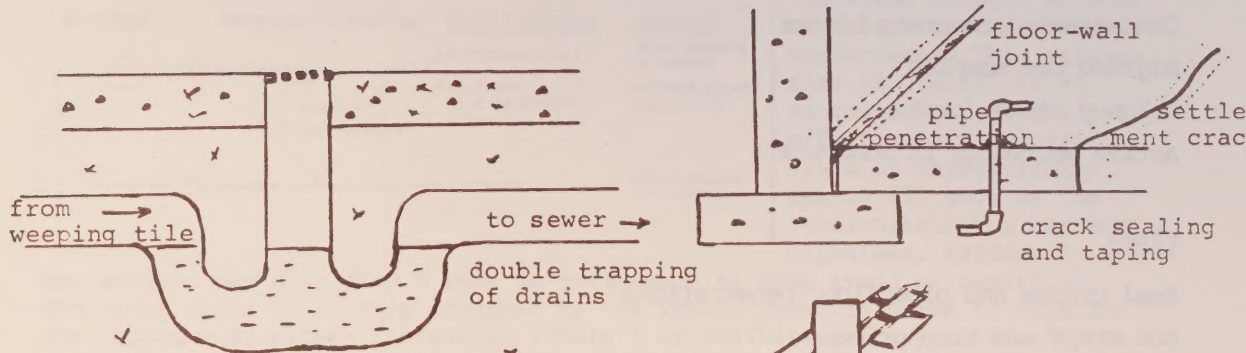
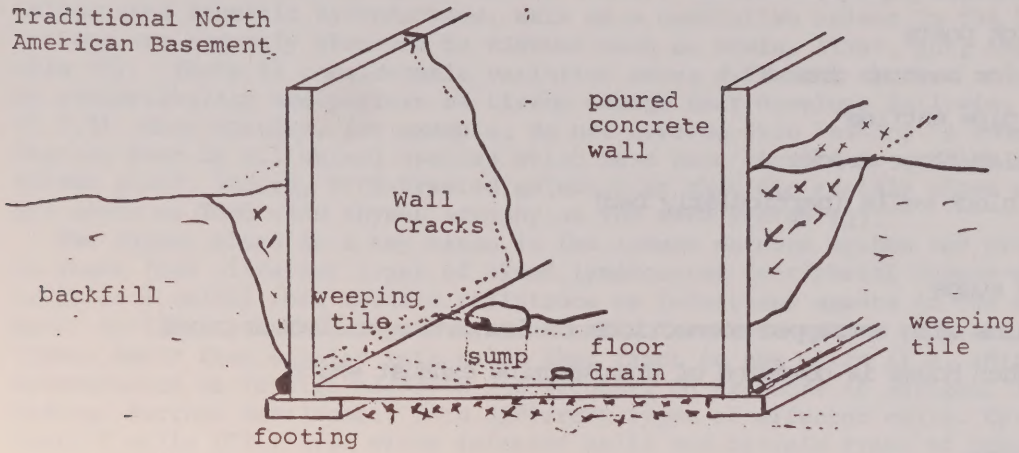
Radon daughter concentrations can be controlled by: a) removing source; b) placing a barrier between the source and the living space; c) diverting the radon before it enters a building; d) modifying the housing air circulation system. All methods have been proven but no one technique is the most cost effective because of widely varying conditions found in older housing.

References

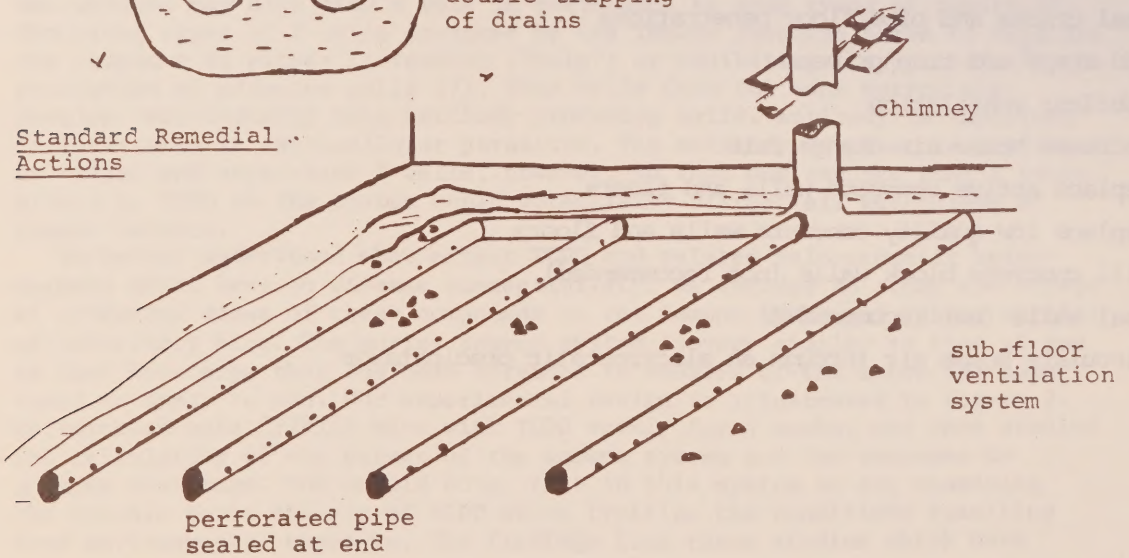
- Culot 1976 - Culot M.V.J., Schiager K.J, and Olsen H.G., 1976, "Prediction of Increased Gamma Fields After Application of a Radon Barrier on Concrete Surfaces", Health Phys. 30, 471.
- AECB Information Bulletin 77-2, April 1977, Criteria for Radioactive Cleanup in Canada (see also news release 77-6).

HOUSING CONSTRUCTION DETAILS

Traditional North American Basement



Standard Remedial Actions



Routes of Entry

Wall and floor cracks

Wall-floor joint

Water and sewer pipe penetration

Hollow jack posts

Recesses for bathtub drains

Fuel oil pipe entries

Furnace slab/floor cracks

Concrete block walls (particularly bad)

Sumps

Drains to sumps

Floor drains with untrapped connections to foundation collector pipes

Windows when house is downwind of uranium mine exhaust shaft

Other sources

Contaminated lumber

Contaminated concrete blocks

Higrade ore samples

Chimney rocks (ore)

Active aggregate in concrete

Fixes

Seal cracks and pipe/floor penetrations

Add traps and trap primers

Subfloor ventilation

Increase house air change rate

Replace active concrete walls and floors

Replace low quality concrete walls and floors

Fill concrete block walls (not recommended)

Seal walls (not recommended)

Circulate house air through an electrostatic precipitator

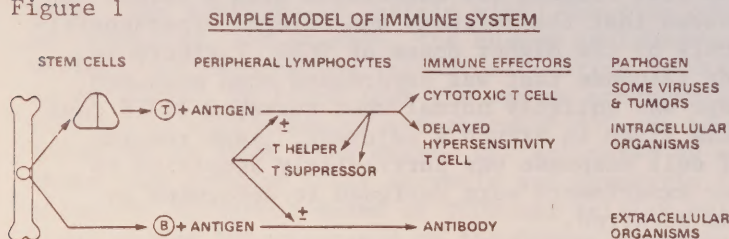
SUPPRESSION OF IMMUNE DEFENCES BY HALOGENATED AROMATIC HYDROCARBONS

David A. Clark, Jack Gauldie, George Sweeney, Host Resistance Program, Departments of Medicine and Pathology, McMaster University, Hamilton, and S. Safe, Department of Chemistry, University of Guelph, Ontario.

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), one of the most toxic of the halogenated aromatic hydrocarbons, acts as a cumulative poison in the body. Lesions are commonly observed in tissues such as brain, liver, gut, and skin (1). There is considerable variation among different species of animals in susceptibility and pattern of tissue damage that develops following TCDD (1,2,3). Many species, for example, do not develop skin lesions. A common feature seen in all animal species which have been studied is atrophy of the thymus gland. Indeed, TCDD-treated guinea pigs that die rapidly after very low doses of TCDD show thymus atrophy as the main lesion (2).

The thymus gland is a key organ in the immune defence system and produces at least four different types of blood lymphocytes (peripheral thymus-derived cells or T cells) that mediate resistance to infectious agents in the environment. As illustrated in figure 1, stem cells from bone marrow emigrate to thymus where they develop into cells that react to the alien (i.e. antigenic) determinants on foreign bacteria and viruses. On exposure to antigen, T cells undergo further development into different types of effector cells. Cytotoxic T cells (CTL) lyse virus infected cells and certain types of tumor cells

Figure 1



(4). T cells which produce delayed hypersensitivity reactions produce soluble mediators that activate macrophages. This activation is crucial if the macrophage is to deal effectively with certain types of intracellular agents (5) such as the tuberculosis and leprosy organisms. Activated

macrophages may also play a role in resistance to some types of tumors (6). Two other types of T cells produced by the immune response serve to regulate the response by either increasing ("help") or inhibiting ("suppression") the production of effector cells (7). Stem cells from the bone marrow also develop independently into antibody producing cells. Antibody is important in resistance to extracellular parasites. The antibody response is regulated by helper and suppressor T cells, however, so that one can see that a toxic effect by TCDD on the thymus could potentially disrupt all mechanisms of immune defence.

To better understand what effect TCDD and related halo-aromatic hydrocarbons might have on disease susceptibility, we decided to study the effect of different doses of these compounds on the immune system of inbred strains of laboratory mice. The murine immune system is very similar to that of man so that knowledge that has been obtained in studies of the mouse has been found to apply to man. Our experimental design is illustrated in figure 2. We injected male C57Bl/6 mice with TCDD weekly for 4 weeks, and then studied the cellularity of the organs of the immune system and the response to antigen challenge. One should note, that in this system we are examining the chronic toxic effects of TCDD which typifies the conditions resulting from environmental exposure. The findings from these studies which have

Figure 2



Table I

	DOSE OF TCDD ($\mu\text{g/kg}$ over 4 weeks)				
	0.4	4	40	100	400
1. Appearance	Healthy	Healthy	Healthy	Sick	Sick
2. Cells in Lymphoid Organs					
Spleen & Lymph Nodes					
Thymus		↓	↓↓	↓↓↓	↓↓↓
3. Type of Immune Response					
Antibody			↓↓↓, ±	ND	ND
Delayed Hypersensitivity		↓	ND	ND	ND
Cytotoxic T Cell	↓↓	↓↓	↓↓	ND	ND

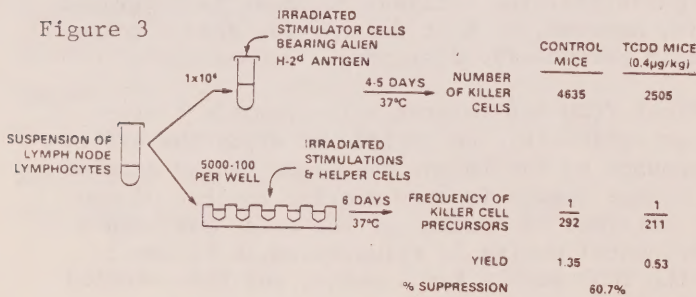
been published in detail elsewhere (8) are summarized in Table I. Doses of 400 $\mu\text{g/kg}$ (400 ppb) and 100 $\mu\text{g/kg}$ depleted cellularity in the thymus and peripheral lymphoid organs (spleen and lymph node) and the animals died. A lower dose of 40 $\mu\text{g/kg}$ (40 ppb) caused cell depletion only in thymus and the animals appeared healthy. No thymus atrophy was seen at 0.4 $\mu\text{g/kg}$. Nevertheless, the proportion of T cells in the peripheral

lymphoid organs was reduced and this finding was associated with a defect in the immune response. Table I shows that the antibody and delayed hypersensitivity responses were affected only by the higher doses of TCDD. Furthermore, we also found that the antibody response that was suppressed when measured 5-7 days after antigen challenge was entirely normal when surveyed 14-15 days after challenge when antigen was given in Freund's adjuvant. These results indicated that the cytotoxic T cell response was particularly sensitive to suppression by TCDD and further experiments were designed to determine by what mechanism this suppression occurred.

Figure 3 illustrates the *in vitro* cell culture method that we used to dissect the effect of TCDD on the murine CTL immune response. Cell suspensions prepared from the lymph nodes, or spleens of normal and TCDD-treated mice, were cultured in test tubes with stimulator cells bearing the H-2^d alloantigen and the number of CTL produced against H-2^d was determined by measuring lysis of antigen-bearing target cells. (% ⁵¹Cr-release cytotoxicity assay). A typical result illustrated to the right in the upper panel of the figure shows that

10⁶ lymph node cells from TCDD-treated mice produced only 2505 units of killer cells whereas the control mouse cells produced 4635 units. It was possible that the reduced CTL production by cells from TCDD-treated mice could have been caused by a toxic destruction of the precursors of CTL. However, in the lower

Figure 3

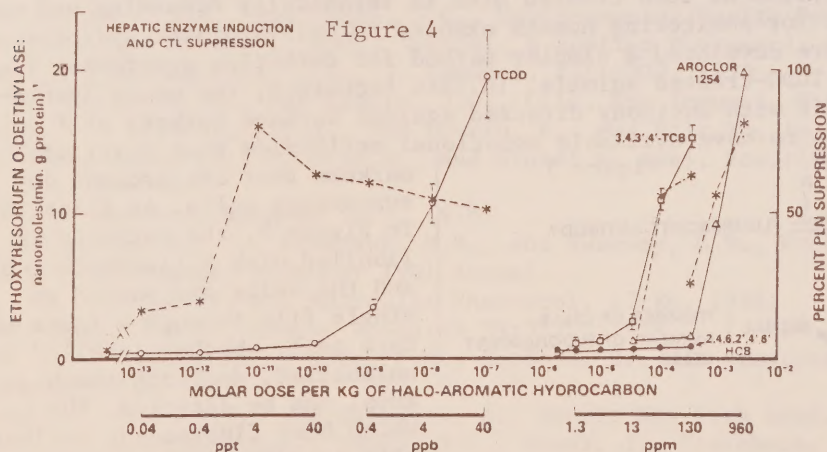


panel of the figure, we actually measured the frequency of precursors by limiting dilution and as can be seen, there was in fact a slight increase in the

frequency of CTL precursors. We used these frequency measurements to calculate the number of precursors that had been added to the tube culture system and determined the yield (units of CTL activity generated per precursor). This figure was reduced by 60.7 % in this experiment in animals treated with 0.4 $\mu\text{g/kg}$ TCDD.

The reduction of CTL generation per precursor after TCDD exposure could be due either to a lack of helper T cells or to an increase in suppressor T cells. Since the thymus appeared to be a key target organ for TCDD toxicity, we conducted some experiments to directly determine if TCDD treatment generated suppressor cells in the thymus. The result from this experiment was been published elsewhere (8). Briefly, we found that thymus cells from mice given a total TCDD dose of 0.4, 0.04, or 0.004 $\mu\text{g/kg}$ became suppressive. Suppression could not be attributed to TCDD itself that might have been present in the thymus. We therefore concluded that TCDD treatment generates suppressor T cells and it would seem from Table I that these suppressor cells act selectively to inhibit only the CTL response.

There is strong evidence that the effects of TCDD are mediated through occupancy of a specific cellular receptor that is genetically controlled. Evidence also suggests that the toxicity of halogenated biphenyls is similarly mediated (9). The receptor is present in many tissues, but in rodents (such as the rat), the highest levels are found in thymus and in the liver (10). When TCDD and related halo-aromatic hydrocarbons interact with the receptor in liver, the activity of certain mixed function oxidase enzymes and cytochromes is increased. For example, the enzyme aryl-hydrocarbon hydroxylase which metabolizes carcinogens (either activating or deactivating them) increases in activity. We found that the enzyme ethoxyresorufin-o-deethylase that is related to activation of cytochrome P₁450 was particularly sensitive to induction by TCDD. This enzyme was activated by doses of TCDD well below those that produce liver necrosis and porphyria (11). Figure 4 shows the effect of different doses of TCDD and related halo-aromatic hydrocarbons on liver enzyme induction and on the immune response. Enzyme induction (left abscissa) is shown by solid lines whereas suppression of the CTL reactivity of lymph nodes (right abscissa) is shown by a dotted line. A TCDD dose of approximately

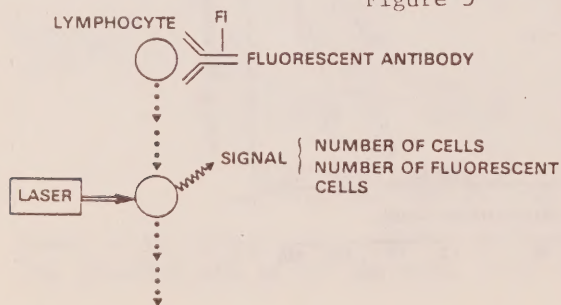


10^{-11} M (0.004 $\mu\text{g/kg}$ or 4 ppt) consistently produced an abrupt onset of suppression. Suppression subsequently declined as the dose of TCDD was increased. It can be readily seen that the onset of immune suppression was a more sensitive measure of the effect of TCDD than was enzyme induction although a slight degree of activation does occur at a dose of 0.004 $\mu\text{g/kg}$. The compound 3,4,3',4'-tetrachlorobiphenyl and Aroclor 1254, a commercial PCB mixture, also induced liver enzymes and immune suppression, although the affinity of these compounds for the TCDD receptor protein is lower so that a greater dose was required to produce a biological effect. In contrast, the compound 2,4,6,2',4',6'-hexachlorobiphenyl that lacks affinity for the TCDD receptor did not produce significant enzyme induction or suppression. The results shown in the figure suggest that the structure of the molecule may affect the toxic effects on liver and thymus in different ways. Thus, low levels of some compounds, such as TCDD, may be much more toxic to the immune system than to liver. It follows that the mechanism of toxicity arises from the nature of the interaction with the receptor in each particular tissue.

Certain strains of mice, such as DBA/2, are less sensitive to TCDD. This "resistance" is attributable to a gene at the "Ah" locus that determines the affinity of TCDD receptor. We have found that DBA/2 mice require 10-100 times more TCDD to cause enzyme induction equivalent to that occurring in C57Bl/6 mice, and that there is a parallel reduction in the sensitivity of the immune system to TCDD. This data provides further support for the idea that immunotoxicity is genetically determined and related to a gene at the "Ah" locus. These findings may have some implications for man. First, different individuals may vary considerably in their sensitivity to TCDD and related halo-aromatic hydrocarbons. Second, extremely low levels of TCDD and related compounds may have significant biological effects. Third, measuring the concentration of a particular halo-aromatic hydrocarbon in fat tissue in the body will provide no information concerning what biological effects may be expected. Fourth, by characterizing the toxicity of different halo-aromatics on different tissues, by identifying the particular halo-aromatic present and by measuring the effect on the immune system, one should be able to predict the effects on other organs.

The culture system shown in Figure 3 that was used to analyze the changes in the immune system of TCDD-treated mice is technically demanding and would not be suitable for monitoring humans exposed to halo-aromatic hydrocarbons. We have therefore developed a simpler method for detecting suppressor T cell stimulation in TCDD-treated animals. In this technique, the mouse lymphocytes are reacted with antibody directed against surface markers of T cells. We are fortunate to have available monoclonal antibodies that react with

Figure 5



markers that are present on suppressor cells. As illustrated in Figure 5, the antibody is labelled with a fluorescent dye, and the cells are passed in single file through a laser beam. Each cell, whether labelled or unlabelled, deflects the beam and thus, can be detected. The cells which bear fluorescent antibody emit an additional signal. We stained lymph node cells from mice with anti-Lyt 1 antibody (which

T CELL SUBSET	MOUSE MARKER	HUMAN MARKER
HELPER T	Lyt 1	OKT 4
SUPPRESSOR T	Lyt 2	OKT 8

is present on helper T cells) or with anti-Lyt 2 (which is present on most T suppressor cells). Our preliminary findings indicate that low levels of TCDD have little effect on the percent Lyt 1+ cells, but significantly increases the number of Lyt 2+ cells. Thus, it may be possible to measure the biological effect of exposure to TCDD by counting suppressor cells using monoclonal antibodies. Further studies are needed to determine if there is a parallel between the amount of suppression measured in vitro, the dose of TCDD, and the number of suppressor cells detected in the blood of mice. Since monoclonal antibodies can now be obtained for human T cell markers, it should be possible to directly apply this method of testing to humans.

Does the activation of suppressor T cells by TCDD predispose to infectious disease? Some studies of human populations exposed to halo-aromatic hydrocarbons has suggested increased frequency of complaints of colds (12,13), and PCBs also have been reported to increase mortality from Duck hepatitis virus (14). Since only the CTL response is suppressed by low dose TCDD, one would anticipate only certain types of infectious agents would be more pathogenic. CTL seem to play a role in resistance to certain types of virus infection (15). Imanishi et al (16) have shown that PCB treatment increases lethality of Herpes virus infection in mice. We wished to know if an increase in susceptibility would occur at doses of TCDD that suppress only the CTL response. Our preliminary findings have shown that TCDD doses of 0.4 and 0.04 µg/kg that have no effect on delayed hypersensitivity or antibody responses do, in fact, increase the mortality following intraperitoneal challenge of C57Bl/6 mice with Herpes simplex type II. Thus, the immunosuppression that we detect following low doses of TCDD may significantly compromise host defences.

Summary and conclusions: (1) TCDD suppresses the immune system of mice and the generation of cytotoxic T cells is uniquely susceptible; (2) Related halo-aromatic hydrocarbons that can react with the genetically controlled TCDD receptor protein in liver and thymus also produce suppression of cytotoxic T cells; (3) The impairment in immunity is due to induction of suppressor cells by low doses of TCDD; (4) Suppression of CTL by these suppressor cells may increase lethality of Herpes virus infections.

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SUPPRESSION OF IMMUNE DEFENCES BY HALOGENATED AROMATIC HYDROCARBONS, David A. Clark, Jack Gauldie, and George Sweeney, Host Resistance Program, Departments of Medicine and Pathology, McMaster University, Hamilton, Ontario, and S. Safe, Dept. of Chemistry, University of Guelph, Ontario.

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), is the most toxic of the halogenated aromatic hydrocarbons. It accumulates in fat depots in the body and damages a number of tissues such as the brain, gut, liver, and skin. Different species of animals vary in susceptibility and pattern of organ damage, but a common feature seen in all animal species which tolerate a sufficient dose, is atrophy of the thymus gland. This organ produces at least 4 types of blood lymphocytes (peripheral thymus-derived cells or T cells) that mediate host defence against infectious agents in the environment.

To better understand the effects that TCDD and related halo-aromatic hydrocarbons might have on disease susceptibility, we have studied the effects of these compounds on the immune system of inbred strains of mice. The murine immune system is reasonably well understood and appears to be quite similar to the human immune system. We injected male C57Bl/6 mice with TCDD weekly for 4 weeks and found that a total dose of 400 µg/kg depleted cellularity in the thymus and peripheral lymphoid organs (spleen and lymph nodes) and the animals died. Lower doses of 40 µg/kg caused depletion only in thymus and the animals appeared healthy, and no thymus atrophy was seen at a dose of 0.4 µg/kg. Nevertheless, at 0.4 µg/kg the proportion of T cells in the peripheral lymphoid organs seemed to be depressed, and this finding was associated with an impairment in the ability of the mice to generate cytotoxic T cells (killer T cells) in an immune response. This defect was seen with doses of TCDD as low as 0.0004 µg/kg, was reproducible at 0.004 µg/kg (4 parts per 10¹²), and was explained by the stimulation of suppressor T cells in the treated animals. There is strong evidence that the effects of TCDD are mediated through occupancy of a specific cellular receptor that is genetically controlled. Evidence also suggests that the toxicity of halogenated biphenyls is mediated similarly. We found that suppression was induced by the halo-aromatic hydrocarbons 3,4,3',4'-tetrachlorobiphenyl and Aroclor 1254, a commercial PCB mixture, but not by 2,4,6,2',4',6'-hexachlorobiphenyl that lacks binding affinity for the genetically controlled TCDD-receptor protein. Interaction between the receptor in liver and TCDD, or related agents, induces mixed-function oxidase enzymes such as arylhydrocarbon hydroxylase and ethoxyresorufin-O-deethylase, and the latter proved to be most sensitive and specific index of induction. Induction of suppressor cells by TCDD proved to be even more sensitive than the enzymatic marker and could be detected by counting the number of cells in lymph node bearing the Lyt 2 marker that is present on suppressor cells. Furthermore, the induction of suppressor cells by low doses of TCDD appeared to correlate with an increased susceptibility to the lethal effects of Herpes simplex virus against which cytotoxic T cells may provide protection. Male mice of the genetically TCDD-"resistant" DBA/2 strain required 10¹-10² more TCDD for induction of liver enzymes and suppressor cells.

- Conclusions:
- (1) TCDD suppresses the immune response and the generation of cytotoxic T cells is uniquely sensitive.
 - (2) Related halogenated hydrocarbons that can react with the genetically controlled TCDD receptor protein in liver and thymus also produce suppression of cytotoxic T cells.
 - (3) The impairment in immunity is due to induction of suppressor cells by low doses of TCDD.
 - (4) Suppression of CTL by these suppressor cells may increase lethality of Herpes virus infection.

10:00 A.M. SPACE 2 SESSION A

PCB SPILL CLEAN-UP NEAR DOWLING, ONTARIO

In November 1973 approximately 1100 gallons of Aroclor 1254 were spilled into sandy soil as the result of a truck/train collision near Dowling, Ontario.

Following initial remedial action, site investigations and citizen action, the Minister of the Environment assigned responsibility for the clean-up to the local municipal government in July 1979.

Further remedial action consisted of the installation of a Hydrodynamic containment well and treatment plant, the alteration of 2.7 acres of drainage, the excavation and treatment of about 3,000 cy. of soil, and a surface treatment of the spill site.

This presentation discusses the problem and its solution from the point of view of a local resident who found himself in the technicalities, the politics and the economics of a complex situation.

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PCB DISPOSAL UPDATE

D. H. Edwards

Waste Management Branch

The question of how Ontario's polychlorinated biphenyls (PCBs) will be disposed of in an environmentally-acceptable manner is still unresolved. At the present time the Waste Management Branch is both funding research and development in this area and also maintaining a close watch on developments in other jurisdictions.

Destruction of the PCB molecule may be accomplished in one of three manners:

- high-temperature thermal destruction;
- chemical destruction (or detoxification);
- other processes.

High-temperature thermal destruction can be achieved by either conventional or innovative methods, and a brief listing under this heading would be:

Conventional Approach

- Rotary kiln
- Co-incineration
- Fluidized-bed reactor
- Sea-borne incineration
(Vulcanus)

Innovative Approach

- Plasma arc
- Plasma torch
- Pyrolysis

The rotary kiln approach is used in some units currently-operating in Europe and the United States, and the use of the cement kiln in Mississauga was a variation considered at one time in Ontario.

The plasma arc and the plasma torch are two research and development processes currently being funded by the Ministry of the Environment in an attempt to secure a mobile destruction system, a concept which is considered much more likely to gain public acceptance than a large stationary destructor.

Chemical destruction has been studied by numerous investigators, and some of the more prominent methods are:

- Goodyear
- University of Waterloo
- B.C. Hydro
- Rockwell
- Sunohio
- Franklin Institute

All of these are either known to involve or believed to involve the use of sodium to strip the chlorine atoms from the PCB molecules. Conditions of reaction vary, as do the means of introducing the sodium into the reaction. In general, however, the use of this technology is probably

limited to low concentrations, i.e. below 10,000 ppm PCB, because of the cost of reagent and the chemical reaction rate achieved.

Other approaches to the PCB destruction problem are:

- Lockheed Microwave
- BASF/Stauffer High-Pressure Incineration
- Diesel engine
- Biological methods
- Ozonolysis.

Of these, only the BASF process is currently operating commercially. Others, such as the Lockheed Microwave, are only at the bench-level of development, and it will probably be a long-time before they ever hold any potential for commercial operation. The use of the diesel engine integrated with an elaborate air pollution control system has been pioneered by D&D Ltd. in Smithville, Ontario. After the completion of a series of tests in the United Kingdom, it is now hoped to complete the testing and evaluation process in Ontario.

Legislation Relating to PCB Use and Disposal

The use of PCBs is federally regulated or controlled by a series of Chlorobiphenyl Regulations drawn under the provisions of the Environmental Contaminants Act, and the provisions of the Transportation of Dangerous Goods Act.

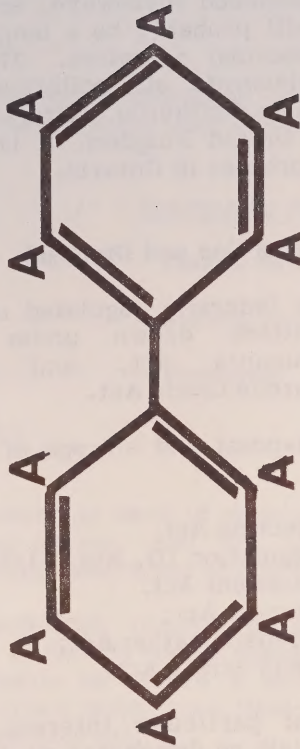
Provincially, the disposal and storage of PCBs is controlled by the following legislation:

- Environmental Protection Act;
- PCB Management Regulation (O. Reg. 11/82);
- Environmental Assessment Act;
- Ontario Water Resources Act;
- Dangerous Goods Transportation Act;
- Occupation Health and Safety Act.

O. Reg. 11/82 is of particular interest since it designates many PCB-contaminated materials as designated wastes and also recognizes that we have neither an approved method of destruction for PCB wastes in Ontario nor a temporary storage facility for PCB waste materials continuously being generated. The regulation also provides a mechanism for owners of PCB wastes to establish an approved PCB waste disposal (storage) site on their property.

POLYCHLORINATED BIPHENYL

PCB DISPOSAL AND MANAGEMENT IN ONTARIO
D. H. Edwards
Waste Management Branch



A - Chlorine substitutions

PCB DESTRUCTION

- HIGH TEMP DESTRUCTION
- CHEMICAL DESTRUCTION
- OTHER PROCESSES

HIGH TEMPERATURE INCINERATION

CONVENTIONAL INNOVATIVE

- ROTARY KILN - PLASMA ARC
- COINCINERATION - PLASMA TORCH
- FLUIDIZED BED - PYROLYSIS
- VULCANUS

CHEMICAL DESTRUCTION

- GOODYEAR
- ROCKWELL
- U. WATERLOO
- B.C. HYDRO
- SUN OHIO
- FRANKLIN INST.

OTHER PROCESSES

- LOCKHEED MICROWAVE
- BASF/STAUFFER H.P. INCINERATION
 - BIOLOGICAL
 - OZONOLYSIS

PROVINCIAL LEGISLATION

- EPA
- DGTA
- EAA
- OHSA
- OWRA

-PCB REGULATION

Chemical Identification and Biological Assay of Polycyclic Aromatic
Hydrocarbons and Other Potential Environmental Mutagens

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Technology Transfer Conference No. 2

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) and related contaminants are found to be widely distributed in the environment. Some of these occur as products of the combustion of fossil fuels and organic matter from anthropogenic and natural sources. These compounds may occur in association with or be adsorbed on soot, fly ash and other forms of atmospheric particulate matter (1,2). Many of these compounds are of concern to public health because of their potential for transformation to carcinogens and mutagens by mammalian microsomal enzymes.

Various theories have been advanced to account for the carcinogenic activity of PAH and their oxidation products in terms of chemical reactivity, structure and charge-transfer processes. In 1955 the Pullmans (3) proposed the concept of the K and L region in order to relate electronic structure and other properties of aromatic molecules with carcinogenic activity. Although some theoretical support for the Pullman theory has been presented by other earlier investigators, at present arene epoxides are considered to be the primary metabolites of PAH, based on the studies of Jerina and his co-workers (4,5). The ultimate carcinogens are believed to be diol epoxides and the carbonium ion at the Bay Region of PAH. Recently, Berger et al. (6) have shown a correlation of electronic reactivity index with carcinogenicity of PAH, whilst Norden et al. (7) believe that statistical data analysis of the structure and chemical activity relationships will be needed to explain the carcinogenic activity of PAH.

In the real world, PAH occur in their normal configuration and also as oxidized or photochemically converted products in association with

particulate matter. PAH may also undergo atmospheric chemical reactions with contaminant gases and other reactive substances such as nitrogen dioxide, sulphur dioxide, sulphur trioxide and hydroxyl radicals.

ANALYTICAL IDENTIFICATION OF PAH

In our laboratories, the PAH content of atmospheric aerosols has been found to be strongly dependent on size distribution, the greater portions of 10 PAH being found in aerosol sizes $\leq 3.0 \mu\text{m}$ (8). A combination of thin layer chromatography (TLC) and fluorescence analysis was devised to resolve and identify 12 different PAH in the extracted organic matter of filtered particulates (9). TLC and spectral analysis (UV, visible and fluorescence) were employed in the quantitative determination of 10 polycyclic quinones (10). The following quinones were identified in samples of suspended particulates from Toronto air: 9,10 anthraquinone; 1,6-, 3,6- and 6,12-benzo(a)pyrene quinones and dibenzo(b,def)chrysene-7,14-quinone. The concentration levels of 10 PAH in particulate air samples from Toronto, Hamilton, Sarnia and Sudbury were determined quantitatively over 3-month periods for 1 year and differences in concentration were related to predominant emission sources (11). In a comparative one-year study of the relative concentrations of 8 PAH in samples collected by conventional high volume sampling and by cascade impactors yielding five particulate fractions of which four were in the respirable sizes of < 1.1 to $7.0 \mu\text{m}$, the size-fractionated samples were found to contain much higher amounts of organic extracts and substantially higher levels of PAH than corresponding high volume samples (12).

Samples of suspended particulate matter collected from the atmosphere of several urban areas in Southern Ontario by staff of the Ontario Ministry of

the Environment were extracted with dichloromethane, concentrated by evaporation in a stream of nitrogen, the residue dissolved in benzene and injected into various packed glass capillary columns for analysis by gas chromatography (GC) and mass spectrometry (MS). As shown in Table 1, a very large number of PAH compounds and derivatives were detected in the environment (13). In many cases the identifications listed in the table are marked (S), as tentative, because positive identification cannot be achieved until the spectra of more authentic standards become available. Many of the compounds listed in the table are present in the data published by other investigators around the world, suggesting the ubiquitous nature of these environmental contaminants. Studies have also been made of the application of chemical ionization MS for analysis of oxidized derivatives of PAH, such as quinones and other species (14).

Five glass columns packed with various different adsorbents were examined for the resolution of mixtures of PAH standards in benzene solution by GC-MS. A glass column developed by Lane, Moe and Katz (15) consisting of 5.4 m, 4 mm I.D., packed with 1% OV-7 on chromosorb W-HP (80-100 mesh) was the only one that achieved full resolution of a mixture of 21 PAH standards into the individual components. After 5 years of use, this column was still able to reproduce its original resolution, as shown in Table 2.

PHOTOCHEMICAL OXIDATION OF PAH

Chemical and photochemical reactions of PAH in the environment apparently represent a major mode of transformation of these compounds. Photochemical oxidation reactions of PAH adsorbed on atmospheric particulates, in the presence of sunlight, result in a variety of products, including the corresponding

Table 1. List of PAH and Derivatives Found by GC-MS in Various Environmental Samples Collected from Southern Ontario

1. Aceanthrylene	33. Dibenzothiophene
2. Acenaphthene	34. Dihydroanthracene(s)
3. Acridine	35. Dihydrobenz(a)anthracene(s)
4. Anthanthrene	36. Dihydrobenzo(a)carbazole
5. Anthracene	37. Dihydrobenzofluoranthene(s)
6. Benz(a)anthracene	38. Dihydrobenzofluorene(s)
7. Benzo(a)anthracenedione(s)	39. Dihydrochrysene(s)
8. Benzindene	40. Dihydrofluoranthene(s)
9. Benzo(a)carbazole	41. Dihydrofluorene(s)
10. Benzo(b)chrysene	42. Dihydrophenanthrene(s)
11. Benzo(b)fluoranthene	43. Dihdropyrene(s)
12. Benzo(ghi)fluoranthene	44. Dimethylacenaphthene(s)
13. Benzo(j)fluoranthene	45. Dimethylantracene(s)
14. Benzo(k)fluoranthene	46. Dimethylbenz(a)anthracene(s)
15. 11-H-Benzo(a)fluorene	47. Dimethylbenzofluoranthene(s)
16. 11-H-Benzo(b)fluorene	48. Dimethylbenzopyrene(s)
17. 11-H-Benzo(c)fluorene	49. Dimethylchrysene(s)
18. Benzo(ghi)perylene	50. Dimethyldibenzofuran(s)
19. Benzo(c)phenanthrene	51. Dimethylphenanthrene(s)
20. Benzo(a)pyrene	52. Diphenylene sulfide
21. Benzo(e)pyrene	53. Diphenylpyridine
22. Benzoquinoline	54. Ethylantracene(s)
23. Binaphthyl	55. Ethylbenz(a)anthracene(s)
24. Carbazole	56. Ethylphenanthrene
25. Chrysene	57. Fluoranthene
26. Coronene	58. Fluorene
27. Dibenzacridine(s)	59. Hydroxyfluorene(s)
28. Dibenzanthracene(s)	60. Indane
29. Dibenzocarbazole(s)	61. Indene
30. Dibenzofluorene(s)	62. Isoquinoline
31. Dibenzofuran	63. Methoxyfluorene
32. Dibenzopyrene(s)	64. Methylacenaphthene(s)

(continued)

Table 1 (cont'd.) List of PAH and Derivatives Found by GC-MS in
Various Environmental Samples Collected from Southern
Ontario

65. Methylanthracene(s)	78. Naphthathionaphthalene
66. Methylbenz(a)anthracene(s)	79. Perylene
67. Methylbenzofluoranthene(s)	80. Phenanthrene
68. Methylbenzofluorene(s)	81. Pyrene
69. Methylbenzophenanthrene(s)	82. Quinoline
70. Methylbenzopyrene(s)	83. Terphenyl
71. Methylcarbazole(s)	84. Tetrahydrophenanthrene
72. Methylfluorene(s)	85. Tetramethylbiphenyl
73. Methylnaphthalene(s)	86. Trimethylanthracene(s)
74. Methylphenanthrene(s)	87. Trimethylfluoranthene(s)
75. Methylpyrene(s)	88. Trimethylphenanthrene(s)
76. Naphthacene	89. Trimethylpyrene(s)
77. Naphthalene	

Table 2. Separation of 21 PAH Standards by Glass Column
of 1% OV-7 on Chromosorb W

Peak Number	Compound	RRT [*] (Found)	RRT ^{**} (Lane)
1	Fluorene	0.547	0.345
2	9-Fluorenone	0.716	0.578
3	Phenanthrene	0.738	0.612
4	Anthracene	0.749	0.625
5	Acridine	0.776	0.665
6	Carbazole	0.811	0.720
7	Fluoranthene	0.962	0.984
8	Pyrene	1.000	1.000
9	11-H-Benzo(a)fluorene	1.063	1.087
10	11-H-Benzo(b)fluorene	1.075	1.101
11	Benz(a)anthracene	1.218	1.274
12	Chrysene	1.225	1.284
13	Naphthacene	1.314	1.304
14	Impurity	-	-
15	Benzo(k)fluoranthene	1.470	1.551
16	Benzo(e)pyrene	1.540	1.638
17	Benzo(a)pyrene	1.564	1.650
18	Perylene	1.592	1.685
19	3-Methylcholanthrene	1.707	-
20	Dibenz(a,h)anthracene	2.065	2.222
21	Benzo(ghi)perylene	2.185	2.345
22	7-H-Dibenzo(c,g)carbazole	2.279	2.455

*RRT = Retention times relative to pyrene

**RRT = Retention times relative to pyrene, reported by Lane et al. (15)

quinones and phenols. Oxygenated derivatives, such as quinones of PAH, have been identified in samples of atmospheric suspended particulates collected on the York University campus (10).

Photooxidation rate studies of benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene, by irradiation with a 500-W quartzline lamp that simulated the UV spectra of sunlight, dark oxidation with 0.2 ppm (by vol.) of ozone in air, and irradiation plus 0.2 ppm ozone, have been published by Lane and Katz (16). More recent studies of photochemical oxidation rates have dealt with anthracene, benz(a)anthracene, dibenz(a,h)anthracene, dibenz(a,c)anthracene, pyrene, and benzo(e)pyrene in the above oxidation reactions. In these experiments by Katz et al. (17), the PAH were adsorbed on Brinkman Cellulose MN-300 precoated TLC plates. The PAH half-lives, in hours, of simulated sunlight photooxidation in air, photooxidation in 0.2 ppm ozone in air and the dark reaction with 0.2 ppm ozone in air are presented in Table 3.

PAH oxidation rates under irradiation with simulated sunlight are considerably increased in the presence of a low concentration of ozone, as shown by the half-lives in Table 3. Anthracene is highly susceptible to oxidation under all above conditions. Benzo(a)pyrene half-life is reduced markedly by ozone oxidation, whereas pyrene, benzo(k)fluoranthene and benzo(b)fluoranthene are comparatively resistant to ozone in the dark reaction.

B(a)P PHOTOLYSIS PRODUCTS

Among the products of B(a)P photolysis in the simulated sunlight irradiation experiments and in irradiation studies in aqueous media, the following three compounds were isolated: 1,6-; 3,6- and 6,12- B(a)P quinones.

Table 3. Half-lives of Polycyclic Aromatic Hydrocarbons under Simulated Atmospheric Conditions

(Expressed in Hours)

	Simulated Sunlight Photooxidation in Air	Simulated Sunlight Air + Ozone (0.2 ppm)	Dark Reaction Ozone (0.2 pp in Air
Anthracene	0.20	0.15	1.23
Benz(a)anthracene	4.20	1.35	2.88
Dibenz(a,h)anthracene	9.60	4.80	2.71
Dibenz(a,c)anthracene	9.20	4.60	3.82
Pyrene	4.20	2.75	15.72
Benzo(a)pyrene	5.30	0.58	0.62
Benzo(e)pyrene	21.10	5.38	7.0
Benzo(b)fluoranthene	8.70	4.20	52.70
Benzo(k)fluoranthene	14.10	3.90	34.90

The structure of these compounds was confirmed by comparison with synthesized standards, using gas chromatography and mass spectrometry. These three quinones of B(a)P were also identified in samples of suspended particulate matter collected from the atmosphere of Toronto by Pierce and Katz (9,10).

STUDIES WITH BIOASSAY SYSTEMS FOR MUTAGENIC ACTIVITY

Ames Salmonella typhimurium assays

In a study by Salamone, Heddle and Katz (18) on the mutagenic activity of 30 PAH compounds isolated from urban air particulates, the following PAH were able to induce a strong, significant increase in the number of His⁺ revertants in the Salmonella/mammalian microsome assay after S-9 activation: benz(a)-anthracene, benzo(a)pyrene, benzo(rst)pentaphene, benzophenanthrene and 3-methylcholanthrene. Weak positive results were obtained with benzo(ghi)perylene, chrysene, 1,2,3,4-dibenzanthracene and 2,3,6,7-dibenzanthracene. Both weakly positive and negative results were obtained with benzo(e)pyrene, coronene, and 7H-dibenzo(c,g)carbazole. The 1,6-; 3,6-; and 6,12-benzo(a)pyrene quinones, isolated as products of photooxidation of benzo(a)pyrene, showed positive activity as direct-acting mutagens (without S-9 activation), but the mixture of the three diones proved to be a strong direct-acting mutagen.

No mutagenic activity was shown by anthracene-9,10-quinone, 1,2-benzanthraquinone, benzanthrone, 3,4,8,9-dibenzpyrene quinone, 1,2-benzofluorene, 2,3-benzofluorene, carbazole, 1,2,5,6-dibenzacridine, 1,2,7,8-dibenzacridine, fluoranthene, perylene and pyrene.

The mutagenicities of two sets of chemical acting singly and in pair-wise combinations were determined by use of the Salmonella/microsomal assay

(Salamone, Heddle and Katz (19)). The first set consisted of the promutagens of benzo(a)pyrene and benzo(rst)pentaphene. The second set contained the direct-acting mutagens methyl-nitro-nitroso-guanidine and ethyl methane sulfonate. In the tests with the promutagens, the quantities of S-9 mix were varied over the range of 0.05 ml to 1.0 ml with increasing quantities of each chemical.

The mutagenic responses or production of revertant colonies of the promutagens, acting singly and in pairwise combinations failed to show an additive effect. Excess quantities of S-9 mix appeared to inhibit partially or totally the mutagenic activity of each chemical, although for each particular dose there was an optimal quantity of S-9 mix to induce maximum activity.

However, the direct-acting mutagens produced, individually, almost linear dose responses with increasing concentrations. In pairwise combinations, these chemicals also showed linear responses that closely approximated the theoretical additivity indicating that the mutagenicity of the mixtures was the sum of the activities of each component.

THE MICRONUCLEUS ASSAY FOR MUTAGENICITY

A modified protocol for the bone marrow micronucleus tests has been described by Salamone et al. (20), consisting of two phases with the incorporation of multiple sampling times. In the first phase, B6C3F1 female mice were injected IP with the chemical at 0 and 24 h, and samples of bone marrow taken at 48, 72 and 96 h. Each treatment consisted of a dose equal to 80% of the LD₅₀. If there was a significant increase in the frequency of micronuclei at any sample

time, the treatment was repeated and the animals sampled at that time in order to confirm the initial result. The agent was classified as clastogenic if the initial positive response was confirmed. If no increase in the micronucleus frequency could be detected in the confirmation test or in phase 1, then a single treatment at either 50% or at both 80% and 40% of the LD₅₀ was given and samples of bone marrow taken at 30, 48 and 72 h (phase 2). Where the response was negative for both phases, the agent was classified as non-clastogenic. However, when an increase in the frequency of micronuclei was noted in phase 2, a confirmation test was performed. In general, when the results of tests from phases 1 and 2 did not agree, a third test was used to reach a decision.

The techniques used to sacrifice the test animals, remove the bone marrow and prepare and score the slides have been described by Heddle and Salamone (21). For each mouse, 500 polychromatic erythrocytes (PCE) were scored and the number of micronucleated PCE recorded. The historical mean frequency of micronuclei per control mouse was 0.642 as based on 173 control mice.

Chemicals

The chemicals used in this study were supplied as 41 coded compounds. This study formed our contribution to an international collaborative program in short-term tests for carcinogens, sponsored by the British Medical Research Council, Imperial Chemical Industries and the U.S. National Institute of Environmental Health Services (22).

The chemicals were prepared fresh daily. DMSO was the principal solvent, with exceptions as noted in the text. In these mice, DMSO was toxic at between 9 and 11 µl/g; accordingly, care was taken to limit the DMSO exposure per

animal to 0.1 ml ($\sim 5 \mu\text{l/g}$). At this level, there was no apparent toxic effect. Though saline was not toxic to the animals, the quantities injected were limited to 2 ml or less so as not to produce any undue stress on the animals.

Micronucleus Results

The micronucleus test results on 41 compounds are presented in Table 4. Twenty agents were detected as clastogens, of which 18 are generally classified as carcinogenic and one, 3-methyl-4-nitroquinoline-N-oxide, is suspect. Twenty-one compounds were not detected as clastogens, nine of these have been classified as carcinogens. These results indicate a detection rate for this modified in vivo protocol of $\sim 68\%$. Though this is slightly below that normally attributable to bacterial assays, especially the Salmonella assay which professes a 70-90% detection rate, it should be noted that the 68% rate obtained here is very reasonable when one considers that (1) positive mammalian in vivo data may be more meaningful than positive bacterial data, especially in estimates of risk to humans, (2) the micronucleus test was designed as a method to detect agents which break chromosomes, not as a method to detect carcinogens, and (3) some carcinogenic agents are tissue specific and thus may not be detectable in bone marrow.

In an earlier study, we did not detect 4NQO, dissolved in DMSO, as a clastogen, even though the highest dose tested was 80% of the $\text{LD}_{50/7}$ (22). In this present study, 4 NQO dissolved in 3% gum arabic was easily detected as a clastogen. The discrepancy in these results is thought to be, in part, solvent related.

Table 4. Micronucleus Assays on 41 Compounds (The Solvent Used for Testing and LD₅₀ Determination was DMSO Unless Otherwise Noted)

Carcinogens Detected as Clastogens	LD ₅₀
2-Acetylaminofluorene	2,220 mg/kg
Benzidine	110 mg/kg
Benzo(a)pyrene	232 mg/kg
Cyclophosphamide	584 mg/kg (saline)
Diethylstilbestrol	551 mg/kg
4-Dimethylaminoazobenzene (Butter yellow)	265 mg/kg
7,12-Dimethylbenz(a)anthracene	84 mg/kg
Dimethyl Carbamoyl Chloride	0.275 mg/kg
DL-Ethionine	-- (saline)
Ethyl Methanesulfonate	367 mg/kg (saline)
Hexamethyl Phosphoramide	1.6 ml/kg
4,4'-Methylene Bis (2-Chloroaniline)	64 mg/kg
N-Methyl-N'-Nitro-N-Nitrosoguanidine	--
Mitomycin C	11 mg/kg (saline)
4-Nitroquinoline-N-Oxide	162 mg/kg (3% gum arabic)
N-Nitrosomorpholine	64 mg/kg
Tris(2,3-Dibromopropyl)Phosphate	1,149 mg/kg (corn oil)
Urethane	1,539 mg/kg
<u>Carcinogens Not Detected as Clstogens</u>	
3-Aminotriazole	--
Auramine (technical grade)	103 mg/kg
Benzo(rst)Pentaphene	> 500 mg/kg
9,10-Dimethylanthracene	--
Epichlorhydrin	0.167 ml/kg
2-Naphthyl Amine	180 mg/kg
β-Propiolactone	0.085 ml/kg
Safrole	0.033 ml/kg
O-Toluidine Hydrochloride	0.338 ml/kg

(continued)

Table 4 (cont'd.) - Micronucleus Assays on 41 Compounds (The Solvent Used for Testing and LD₅₀ Determination was DMSO Unless Otherwise Noted)

Non-Carcinogens Not Detected as Clastogens	LD ₅₀
4-Acetylaminofluorene	364 mg/kg
Anthracene	> 450 mg/kg
Benzo(ghi)Perylene	> 500 mg/kg
γ-Butyrolactone	0.875 ml/kg
4-Dimethylaminoazobenzene-4 Sulphonic Acid Na Salt	132 mg/kg
Dimethyl Formamide	3.4 ml/kg
Dinitrosopentamethylene Tetramine	110 mg/kg
Diphenylnitrosamine	1,110 mg/kg
1-Naphthylamine	96 mg/kg
Pyrene	514 mg/kg
3,3', 5,5'-Tetramethylbenzidine	135 mg/kg
1,1,1-Trichloroethane	0.063 ml/kg
<u>Non-Carcinogens Detected as Clastogens</u>	
Azoxybenzene	115 mg/kg
3-Methyl-4-Nitroquinoline-N-Oxide	318 mg/kg

With in vitro systems, PAH have been tested fairly extensively. In particular, the mutagenicity of some 40-50 have been examined with the Salmonella assay (18,23,24). In contrast, only about 9 or 10 PAH have been tested in the in vivo mutagenicity assays. Table 5 lists all PAH that have been tested on in vivo micronucleus assays (25) and compares the micronucleus mutagenicity data with published Salmonella mutagenicity data. A major factor contributing to the paucity of PAH testing with in vivo mutagenicity assays is that PAH are inherently non-toxic in animal systems while the optimal PAH solvents are

extremely toxic. Thus, either DMSO, corn oil or gum arabic is generally used as a solvent. Of these three, DMSO is the best PAH solvent. However, DMSO is fairly toxic in itself, having an LD₅₀ between 9 and 11 ml/kg body weight. Therefore, treating animals with PAH for mammalian in vivo tests such as the micronucleus, abnormal sperm head or sister chromatid exchange, often involves injecting slurries.

In some cases when PAH yield in vivo non-mutagenic results, it is possible that higher doses of chemical might have yielded a positive effect. However, the chemical, due to its toxicity, could not be administered in sufficient quantity to induce that endpoint. As shown in Table 5, only 2 PAH were detected as clastogens. Of the 5 PAH not detected as clastogens, 9,10-dimethylantracene and benzo(rst)pentaphene have been classified as carcinogenic as well as mutagenic in in vitro studies. The negative clastogenic results for these two chemicals may signify that the mutagenic endpoint of these chemicals is not that of chromosome breakage or that the chemical shows no bone marrow specificity. However, both chemicals are relatively non-toxic as neither chemical could be given in sufficient quantity, even as a slurry, to kill any of the treated animals. Therefore, the negative results may also mean that neither compound has been tested at a high enough dose necessary to reach the target tissue and induce damage. This reinforces the concept that negative in vivo data should be accepted with reserve until confirmed by tests on other target tissue. On the other hand, positive in vivo mutagenic information is meaningful in denoting potential genetic effects.

Table 5. Assays of PAH for Mutagenicity

Compound	Carcinogenicity	Assays for Mutagenicity	
		Ames Salmonella	<u>In Vivo</u> Micronucleus
Anthracene	-	-	-
Benzo(rst)Pentaphene	+	+	-
Benzo(ghi)Perylene	-	+	-
Benzo(a)Pyrene	+	+	+
9,10-Dimethylantracene	+	+ ^a	-
7,12-Dimethylbenzanthracene	+	+ ^b	+
3-Methyl Cholanthrene	+	+	- ^c
Phenanthrene	-	- ^b	- ^d
Pyrene	-	-	-

+ Positive mutagenic result

- Negative mutagenic result

a Simons and Sheppard (26)

b McCann et al. (24)

c Bruce and Heddle (27)

d Bayer (28)

In Vitro and In Vivo Assays - Pairwise Combinations

In the working and living environment, man is frequently exposed to potentially genotoxic pollutants. This exposure may consist of simple chemical agents but, more generally, the effects are due to the action of a combination of chemicals that contaminate the air and water environment as complex mixtures. Such mixtures include substances that are not mutagenic as well as promutagens and direct acting mutagens. The biochemical interactions of these mixtures on living systems are difficult to assess because the biological effects may be due to the occurrence of dominant multiple reactions that represent additive, synergistic or antagonistic influences.

Estimates of genetic risk to the human population from environmental and man-made chemicals must be based on knowledge of a substance's mutagenic potency. Frequently, the assays used to determine this potency are bacterial tests to which exogenous mammalian enzymes have been added in order to activate promutagens. In these experiments the activation system has been shown to be an important variable which may affect the results both quantitatively and qualitatively, thus making the extrapolation of these results to man difficult. The use of in vivo assays, each of which possesses an endogenous activation system, may provide a better appraisal of the mutagenic potency. However, the evaluation of mutagenic potency is further complicated by the fact that human exposure characteristically involves complex mixtures rather than pure compounds. To obtain some insight as to how in vitro and in vivo assay systems respond to mixtures, we have studied several mutagens singly and in simple model mixtures (pairwise combinations), using both the in vitro Salmonella/mammalian microsome assay and the in vivo mouse bone marrow micronucleus assay.

In the case of the studies of pairwise combinations with the Salmonella/microsome assay, the promutagens were treated with the aroclor 1254 induced metabolic activation complex (S-9). The exogenous activation system is an important variable which may affect the results both quantitatively and qualitatively (Salamone et al. (19)). Combination experiments with the promutagens, benzo(a)pyrene (BaP), benzo(rst)pentaphene (B(rst)Pe) and diamino-anisole (DAA) consisted of a single dose of BaP and increasing doses of B(rst)Pe or a single dose of DAA and increasing doses of BaP or B(rst)Pe. In each case the combinations of the promutagens were non-additive (Table 6).

The Salmonella combination studies with the direct acting mutagens methyl-nitro-nitroso guanidine (MNNG), ethyl methane sulfonate (EMS), methyl methane sulfonate (MMS) and acriflavin, indicated dose-responses that compared favourably with the predicted additive values derived from individual dose-effect data, in the absence of S-9. When 0.2 ml of S-9 was added to the reaction mixture of MMS and acriflavin, the results were less than additive.

Studies of pairwise combinations on the in vivo mammalian bone marrow micronucleus assay, with B6C3F1 female mice (Table 7), indicated that with the direct-acting mutagens, MNNG and EMS, the dose-response was additive. Furthermore, the combination of BaP and cyclophosphamide (CP), with different modes of endogenous activation produced an additive dose response. On the other hand, the expected additive dose-response of CP and dimethylbenzanthracene (DMBA) was not attained, as the result was not statistically significant. The response of the pairwise combination of the promutagens BaP and DMBA was non-additive, as expected (30).

More studies of pairwise combinations and complex mixtures will be required to elucidate the impact of similar or different metabolic pathways

on mutagenicity with in vivo systems. It is believed that in vivo systems should provide a better appraisal of mutagenic damage in mammalian tissues than tests with in vitro systems.

Effects of Solvents on Toxicity and Mutagenicity

We have noted that the toxicity and mutagenicity of a particular compound is at times related to the solvent used. This relationship has been investigated for five different compounds. In each case, DMSO was employed as one of the solvents, the other solvents being saline for cyclophosphamide (CP), ethyl methane sulfonate (EMS) and mitomycin C (MMC); while corn oil was used for 9,10-dimethyl-1,2-benzanthracene (DMBA), 3% gum arabic for 4-nitroquinoline-N-oxide (4-NQO) and water for ascorbic acid.

The solvent effect on mutagenicity was determined on the bone marrow micronucleus assay by use of both time-response and dose-response data for five chemicals dissolved in the solvents indicated in Table 8. Ascorbic acid was not tested as it is not considered to be a mutagen, though it has been shown to induce His⁺ reversions in Salmonella by Stich (29). For the time-effect response, the mice were injected with a single dose of the chemical in either solvent at a given fraction of the LD₅₀ and samples of bone marrow were tested at various times after the injection. For the dose-effect response, the animals were given 5 doses of each chemical in either solvent, each dose equivalent to a fraction of the LD₅₀.

Table 6. Mutagenic Activity of Pairwise Combinations of Model Agents on Salmonella Bacterial Assay

Pairwise Combination	Types of Mutagens	Activation Complex, S-9	Response
BaP + B(rst)Pe	Promutagens	with S-9	non-additive
MNNG + EMS	direct acting	none	additive
MMS + acriflavin	direct acting	none	additive
MMS + acriflavin	direct acting	with S-9	less than additive
DAA + BaP	promutagens	with S-9	non-additive
DAA + B(rst)Pe	promutagens	with S-9	non-additive

benzo(a)pyrene, BaP; benzo(rst)pentaphene, B(rst)Pe;
methyl-nitro-nitroso-guanidine, MNNG; ethyl methane sulfonate, EMS;
diaminoanisole, DAA; methyl methane sulfonate, MMS

Table 7. Mutagenic Activity of Pairwise Combinations of Model Agents on In Vivo Bone Marrow Micronucleus Assay

Pairwise Combination	Types of Mutagens	Mode of Activation	Response
EMS + CP	direct acting + promutagen		additive
EMS + MNNG	direct acting		additive
EMS + BaP	direct acting + promutagen	different modes	additive
BaP + cyclophosphamide (CP)	promutagens	different modes	additive
BaP + dimethylbenzanthracene (DMBA)	promutagens	similar	non-additive
CP + DMBA	-	different modes	additive response, not statistically significant

Table 8. Effect of Solvent on Chemical Toxicity and Mutagenicity

Chemical	LD ₅₀ (mg/kg)		<u>Toxicity</u>	Mutagenic Time-Dose Effect Response
	Solvent 1 DMSO	Solvent 2	% Difference in LD ₅₀	
DMBA	71	107 ^a	50	Greater in DMSO 3.5 x at 48% LD ₅₀
CP	424	584 ^b	38	2 x greater in saline at 20% LD ₅₀
EMS	134	367 ^b	139	1.7 x greater in saline
4NQO ^e	16	162 ^c	966	6 x greater in gum arabic
MMC	8.8	10.7 ^b	17	none
Ascorbic acid	643	5000+ ^d	> 674	not tested

^a corn oil

^b saline

^c 3% gum arabic

^d water

^eLD₅₀ values based on a 4-day rather than 7-day mortality pattern

The toxicity data indicate that the toxic effect of each chemical is greater when DMSO is used as the solvent. The solvent-related effect on toxicity showed the least difference for MMC in saline versus DMSO, while the greatest differences were noted for 4NQO (3% gum arabic) and ascorbic acid (water).

No solvent effect on the mutagenicity of MMC was observed. This is as might be expected, since the difference in toxicity induced by the two solvents was minor. On the other hand, EMS induced a slightly greater mutagenic time- and dose-effect response with saline as the solvent. A similar result was

observed for cyclophosphamide. The greatest solvent related mutagenic effect was produced with 4NQO. In gum arabic, the mutagenic response of 4NQO in DMSO at 30% of the LD₅₀ is comparable to the mutagenic response of 4NQO in DMSO at 180% of the LD₅₀. However, the results with DMBA are directly opposite those obtained for the other compounds. DMBA was more mutagenic in both the time- and dose-effect experiments when dissolved in DMSO. These data suggest that though there appears to be a definite relationship between the solvent of choice and the observed toxicity, no clear relationship exists between the solvent used and the mutagenicity observed. The EMS, CP and 4NQO data exemplify cases where the greater mutagenicity was associated with the solvent which at a given percent of the LD₅₀ allows the most material to be administered safely to the animal. However, with DMBA, the greater mutagenicity was associated with the most toxic solvent. Whether these responses are consistent when other mammalian endpoints, such as SCE and abnormal spermhead morphology are tested, is still to be determined.

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Summary of Nine Years of Investigation of Sewage Sludge on Land
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This report summarizes the results of a research program, conducted between 1972 and 1980, on land application of fluid sewage sludge. Most of the sludges used resulted from the chemical treatment of sewage with calcium hydroxide, ferric chloride and aluminum sulphate for P removal. The objective was to determine safe rates of sludges which may be applied to agricultural soils without polluting ground and surface waters with elements or micro-organisms pathogenic to humans and animals, and without reducing the quantity or quality of the crops produced.

The various phases of the research involved (i) runoff studies with fall, winter and spring applied sewage sludge, (ii) microbial studies, (iii) nitrogen availability studies, (iv) rate and source of sludge field studies with corn and brome grass, (v) a greenhouse study on metal uptake from sewage sludges, (vi) a greenhouse and laboratory experiment for the selection of a chemical extractant for plant available heavy metals in polluted soils, and (vii) pedological examination and characterization of soils treated with sewage sludges.

Runoff studies

Nitrogen and phosphorus losses in runoff from sludge treated plots was quite small as shown on Tables 1 and 2. Losses of metals were also very small and are not presented. One exception in runoff losses occurred when heavy rain fell immediately after sludge application. In this case there was appreciable movement of the sludge.

We conclude that runoff losses of nutrients and metals can be restricted to acceptable levels if sludges are (i) applied at low rates (not exceeding 1.5 cm per application), (ii) are applied not less than 48 hours before heavy rains are predicted, and (iii) are not applied on steep slopes or near waterways. In winter, sludge should not be applied on ice or frozen soil, or, if a significant thaw is predicted within 48 hours, on snow-covered ground.

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Microbial studies

Fluid digested sewage sludges contained considerable numbers of total and faecal coliforms and faecal streptococci, Table 3. Sewage sludge application on crop land did not result, however, in greatly increased numbers of the indicator micro-organisms in runoff waters, Table 4.

Salmonella was detected in 20 of 54 sludge samples, in one of 484 runoff samples and in six of 207 plant samples examined. Pathogens in sludge are not a hazard if sludge is applied with recommended precautions.

Nitrogen studies

About 60% of the ammonium nitrogen in sludge applied on the soil surface was lost by volatilization, Table 3. Organic N in sludge was capable of being rapidly mineralized and nitrified in soil. The chemicals used in sewage treatment had no apparent effect on N mineralization and nitrification. Sludge application in excess of the crop's nitrogen requirement resulted in accumulation of excess N in the soil. Total N in sludge was approximately half as available as N contained in ammonium nitrate fertilizer. This is similar to the availability expected for cattle or hog manure.

Source and Rate of Sludge in Field and Greenhouse Studies

A greenhouse experiment was run in which annual ryegrass was grown for 14 crops with several rates of six different sludges applied and worked into the soil before seeding of each crop. In the field experiments corn was grown on a loam soil at the Elora research station and on a loamy sand at the Cambridge research station and brome grass was also grown on the loam soil. These crops were grown for 8 years with three sewage sludges applied each year at a series of rates compared with nitrogen and phosphorus provided from commercial fertilizers.

Moderate rates of sewage sludge produced at least as high yields of corn and brome grass as ammonium nitrate and phosphate fertilizers. Sludge application markedly increased sodium bicarbonate soluble (plant available) soil phosphorus, Table 5.

Cadmium, copper, nickel, zinc and molybdenum concentrations in the ryegrass, brome grass and corn stover (stalks, plus leaves at time of grain harvest) were increased by high rates of sewage sludge high in those metals. Metal concentrations in corn grain were less affected by treatment than concentrations in the stover. In the greenhouse study one particularly high copper sludge caused copper toxicity to ryegrass when applied at high rates.

The calcium sludge increased soil pH and reduced the effect of metals in sludge on content in the crops. Chromium concentration in corn stover was increased significantly after several years of application of one sludge which was high in chromium. Cobalt, mercury, lead and selenium concentrations in the crops were not affected by application of sewage sludges but the sludges used did not contain unusually high concentrations of any of these metals except lead.

Cadmium concentrations in ryegrass from the greenhouse experiment are presented in Table 7 and concentrations in corn stover in Table 8. Although high rates of the Guelph sludge, which is high in cadmium, markedly increased cadmium content of the ryegrass, high rates of the low cadmium North Toronto sludge did not increase cadmium content measurably. One puzzling result of those studies is the consistently high content of cadmium in ryegrass which only received the first application of sludge (Table 7). Corn stover cadmium concentrations in the loamy sand were consistently higher than in the loam soil (Table 8).

Zinc concentration in ryegrass increased with increasing rates of the zinc-rich Sarnia sludge and the zinc concentration increased from crop to crop with repeated applications of sludge, Table 8. Similar patterns were observed in the field. Nickel and copper in the crops followed patterns more similar to those with zinc than to cadmium.

Cadmium, copper, nickel, zinc and molybdenum concentrations in crops increase when sludges high in these metals are applied at high rates of application. These studies provide conclusive evidence, however, that sludges which contain metal concentrations acceptable under the Ontario guidelines when applied to soils at recommended rates will leave a comfortably wide margin of safety in the metal content of field and vegetable crops. This will be true provided the sludges are applied to soils of pH 6.0 or above and provided the metal concentrations in the soils are not unacceptably high before sludge is applied.

Soil Tests for Plant Available Heavy Metals

A greenhouse study was conducted on 45 Ontario soil materials obtained from sites which exhibited a range of levels of metal contamination developed over a period of years near metal smelters, from snow dumping sites and sites where sludge had been applied over a period of years. Metal concentrations in Swiss Chard grown on these soils were related to the amounts of metals extracted by different chemical solutions which have been

suggested for measuring the amounts of soil metals available to plants. Suitable extractants were found for cadmium, zinc and nickel. None of the extractants was suitable for copper. Details of this study have been published (Haq et al, 1980).

Publications

Greater detail on this research is provided in the published reports and scientific papers listed in this report.

Published Reports

- A. Canada-Ontario Agreement Reports dealing with the program*:
1. "Land Application of Sewage Sludge", Research Report No. 1, 1973.
 2. "Land Disposal of Sewage Sludge", Volume I, Research Report No. 16, 1975.
 3. "Land Disposal of Sewage Sludge", Volume II, Research Report No. 24, 1975.
 4. "Land Disposal of Sewage Sludge", Volume III, Research Report No. 35, 1976.
 5. "Land Disposal of Sewage Sludge", Volume IV, Research Report No. 60, 1977.
 6. "Land Disposal of Sewage Sludge", Volume V, Research Report No. 73, 1978.
 7. "Land Disposal of Sewage Sludge", Volume VI, Research Report No. 90, 1979.
 8. "Land Disposal of Sewage Sludge", Volume VII, Research Report No. 98, 1980.
- B. Scientific publications arising from this program:
1. Bates, T.E., A.U. Haq, Y.K. Soon and J.R. Moyer, 1975. "Uptake of Metals from Sewage Sludge Amended Soils", in Proc. Int. Conf. Heavy Metals in the Environment. Vol. II, October 27 to 31, 1975, Toronto, Canada, pp. 403-416.
 2. Beauchamp, E.G., G.E. Kidd, and G. Thurtell. 1978. "Ammonia Volatilization from Sewage Sludge Applied in the Field", J. Environ. Qual. 7:141-146.
 3. Soon, Y.K., T.E. Bates, E.G. Beauchamp and J.R. Moyer. 1978. "Land Application of Chemically Treated Sewage Sludge: I. Effects on Crop Yield and Nitrogen Availability", J. Environ. Qual. 7:264-269.

* Research Reports may be obtained from Training and Technology Transfer Division (Water), Environmental Protection Service, Environment Canada, Ottawa, Ontario K1A 1C8, or Ontario Ministry of the Environment, Pollution Control Branch, 135 St. Clair Avenue West, Toronto, Ontario M4V 1P5.

4. Soon, Y.K., T.E. Bates, and J.R. Moyer. 1978. "Land Application of Chemically Treated Sewage Sludge: II Effects on Plant and Soil Phosphorus, Potassium, Calcium and Magnesium and Soil pH", J. Environ. Qual. 7:269-273.
5. Beauchamp, E.G., Y.K. Soon, and J.R. Moyer. 1979. "Nitrate Production of Chemically Treated Sewage Sludges in Soil" J. Environ. Qual. 8:557-560.
6. Soon, Y.K., T.E. Bates, and J.R. Moyer. 1980. "Land Application of Chemically Treated Sewage Sludge: III Effects on Soil and Plant Heavy Metal Content", J. Environ. Qual. 9:497-504.
7. Haq, A.U., T.E. Bates, and Y.K. Soon. 1980. "Comparison of Extractants for Plant Available Zn, Cd, Ni and Cu in Ontario soils", Soil Sci. Soc. Am. J. 44:772-777.
8. Webber, M.D., Y.K. Soon, and T.E. Bates. 1981. "Lysimeter and Field Studies on Land Application of Wastewater Sludges". Prog. Wat. Tech. 12:905-917.
9. Soon, Y.K. 1981. "Solubility and Sorption of Cadmium in Soils Amended with Sewage Sludge", J. Soil Sci., 32:85-95.
10. Lee, C.C., Y.K. Soon, and T.E. Bates. 1981. "Phosphate Adsorption by Soil Amended with Chemically Treated Sewage Sludges". Can. J. Soil Sci. 61:165-168.
11. Remmen, S.F., T.E. Bates, Y.K. Soon and A.U. Haq. "Extractability of Heavy Metals in Sludge and in Soil Amended with Sewage Sludge". J. Environ. Qual. (submitted for publication).
12. Remmen, S.F., T.E. Bates, Y.K. Soon and A.U. Haq. "Growth and Metal Uptake of Ryegrass Grown on Soil Amended with Sewage Sludge". J. Environ. Qual. (submitted for publication).

Table 1: Total Nitrogen Losses in Runoff, 1973 to 1977.

Time of Sludge Application	Winter Runoff		Summer Runoff	
	2% slope	6% slope	2% slope	6% slope
Nitrogen - kg/ha per year				
No sludge	1.3	1.7	3.2	4.1
Mid November	2.0	2.9	1.8	6.1
Mid January	3.6	8.1	2.3	4.3
Late April	1.4	1.8	2.8	4.3

Table 2: Total Phosphorus Losses in Runoff, 1973 to 1977.

Time of Sludge Application	Winter Runoff		Summer Runoff	
	2% slope	6% slope	2% slope	6% slope
Phosphorus kg/ha per year				
No sludge	0.4	0.5	0.9	1.5
Mid November	0.5	0.7	0.4	2.0
Mid January	0.7	1.3	0.6	1.5
Late April	0.3	0.4	0.7	1.7

Table 3: Most probable number of some indicator organisms per 100 ml in North Toronto (iron-treated) sludge.

Micro-organisms	Samples of:					
	May 9/73	May 19/73	May 25/73	May 29/73	June 23/73	July 26/73
Total Coliforms	155,000	480,000	795,000	19,500,000	165,000	1,900,000
Faecal Coliforms	20,000	12,500	80,000	2,400,000	80,000	24,000
Faecal Streptococci	2,300,000	445,000	895,000	6,000,000	295,000	7,300,000

Table 4: Average numbers of indicator organisms in runoff waters.

Indicator Microorganisms	Time and rate of sludge application (kg N/ha)				
	NONE		FALL(200)	WINTER (200)	SPRING (200)
	2	6	6	6	6
Most probable number/100ml Runoff event of April 2, 1974					
Total coliforms	65,000	805,000	455,000	417,000	51,000
Faecal coliforms	2	1	1	0	3
Faecal Streptococci	2,400	9,100	27,000	37,000	140,000
Runoff event of May 17, 1974†					
Total coliforms	100	93	1,200	2,500	795
Faecal coliforms	0	0	10	0	32
Faecal Streptococci	1,100	790	28,500	8,000	2,400

† The spring 1974 application was on May 3.

Table 5: Daily losses of ammonia volatilized during the May and October experimental periods.

May Experiment		October Experiment	
Date	NH ₃ -N volatilized	Date	NH ₃ -N volatilized
	kg/ha		kg/ha
8*	22.2	8†	16.4
9	36.5	9	14.5
10	14.5	10	4.2
11	8.9	11	4.5
12	5.4	12	3.9
13	3.5	13	2.0
		14	3.2
		15	1.6
Total	90.9	Total	50.3

* measurements began at 1300 h, 150 kg ammonium N added/ha

† measurements began at 1200 h, 89 kg ammonium N added/ha

Table 6: Sodium bicarbonate extractable phosphorus in surface soil (0-15 cm) of the corn experiment on Conestoga loam, 1974 to 1980.

Year	Source and rate of N (kg N/ha)			
	Ammon. Nitrate 100	Calcium sludge 200	Aluminum sludge 200	Iron sludge 200
µg P/g*				
1974	11de**	33b-e	17b-e	14cde
1975	28fg	56cde	31fg	27fg
1976	30f	87c-f	57ef	53ef
1977	53efg	73def	57efg	60efg
1978	27g	112de	50fg	47fg
1979	34f	118cd	53e	60e
1980	40f	102d	68e	70e

* Treatment means in any one row not followed by a common letter are significantly different at 0.05 probability by Duncan's Multiple Range test.

** Phosphorus fertilizer was added to the ammonium nitrate treatment.

Table 7: Cadmium concentration in crops 1 to 14 of ryegrass receiving sewage sludges from Guelph and North Toronto before each crop.†

Crop	Control (NH ₄ NO ₃)	Guelph			North Toronto		
	200	200	1600	1600§	200	1600	1600§
µg Cd/g							
First	0.55	1.03	2.60	2.60	0.70	0.85	0.85
Second	0.35	1.10	5.61	5.61	0.45	0.40	0.40
Third*	0.40	0.65	2.45	2.45	1.45	0.70	0.70
Fourth	0.31	0.86	3.14	3.14	0.38	0.44	0.44
Fifth*	0.60	0.95	3.70	3.70	0.50	0.65	0.65
Sixth	1.31	2.05	5.20	3.75	1.00	0.50	0.55
Seventh*	1.40	2.08	6.18	6.88	0.89	0.75	1.00
Eighth	1.05	2.40	8.05	8.00	0.85	0.90	0.95
Ninth*	1.83	1.77	3.58	5.19	0.42	0.43	0.54
Tenth	2.25	2.33	4.51	6.60	0.67	0.85	0.85
Eleventh*	2.00	2.20	7.02	4.89	0.68	1.00	0.81
Twelfth	1.05	2.55	8.30	7.50	0.48	0.38	0.48
Thirteenth*	1.01	1.72	3.65	4.84	0.49	1.02	0.66
Fourteenth	0.98	2.35	2.20	5.55	0.40	0.70	0.48

† The sludge from Guelph supplied the greatest amount of cadmium in the experiment, while the cadmium content of the North Toronto sludge is near the average of the sludges used.

§ No sludge application after the fifth crop.

* Plots were leached after sludge application but before seeding.

Table 8: Cadmium concentration in corn stover from 1973 to 1980.

Year	N source and rate (kg N/ha)				
	Ammon. Nitrate 100	Calcium sludge 200	Aluminum sludge 200	Aluminum sludge 1600	Iron sludge 200
µg Cd/g					
<u>Conestoga loam, Elora</u>					
1973	0.23b*	0.30ab	-	0.40ab	0.38a
1974	0.28abc	0.37abc	0.38abc	0.46ab	<u>0.54a†</u>
1975	0.24d	0.43cd	0.35cd	0.67ab	<u>0.80a</u>
1976	0.30def	0.43cde	0.33def	<u>0.67a†</u>	0.70a
1977	0.21ef	<u>0.35de†</u>	0.34cde	<u>0.77a</u>	0.53b
1978	0.13g	0.25de	0.24def	0.71a	0.36c
1979	0.16e	0.16e	<u>0.31cd†</u>	0.97a	0.39c
1980	0.11g	0.18efg	<u>0.29de</u>	1.41a	0.57c
<u>Caledon loamy sand, Cambridge</u>					
1973	0.38b	0.60a	--	--	0.64a
1974	0.36bc	0.86ab	0.42bc	0.67abc	<u>1.09a†</u>
1975	0.43ab	0.55ab	0.33ab	0.47ab	<u>0.36ab</u>
1976	0.43fg	<u>0.63c-g†</u>	0.53d-g	<u>1.03ab†</u>	1.13a
1977	0.37de	<u>0.44cde</u>	0.44cde	<u>0.90ab</u>	0.72bc
1978	0.24e	0.35de	0.44cd	1.29a	0.91bc
1979	0.31ef	0.26f	<u>0.54de†</u>	1.33a	0.88bc
1980	0.23fg	0.24fg	<u>0.43cde</u>	1.49h	0.70a

* Individual treatments in any one row not followed by a common letter are significantly different at 0.05 probability level by Duncan's Multiple Range Test.

† Indicates that the Ontario sludge guideline for maximum Cd addition to the soil was exceeded.

Table 9: Zinc concentration in crops 1 to 14 of ryegrass receiving sewage sludge from Sarnia before each crop.

Crop	Ammonium Nitrate	Sarnia Sludge			
		kg N/ha			
	200	200	800	1600	1600§
µg Zn/g					
First	43	59	167	241	241
Second	38	105	218	211	211
Third*	31	92	146	245	245
Fourth	32	64	156	103	103
Fifth*	33	44	122	165	165
Sixth	51	104	292	490	303
Seventh*	36	99	209	426	343
Eighth	33	177	309	530	318
Ninth*	36	102	275	459	191
Tenth	32	117	420	591	163
Eleventh*	55	136	553	784	153
Twelfth	16	144	390	447	117
Thirteenth*	16	126	349	648	208
Fourteenth	12	134	328	492	173

* Indicates pots were leached after sludge application but before seeding.

§ No sludge application after the fifth crop.

HEAVY METAL CONTENTS OF FIELD AND
VEGETABLE CROPS GROWN ON SOILS TREATED
WITH SEWAGE SLUDGE

by

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ABSTRACT

Field and vegetable crops were grown on sludge treated soils in lysimeters at Environment Canada's Wastewater Technology Centre, Burlington. Heavy metal concentrations in the crops are compared and some factors affecting the concentrations are discussed.

Sludge treatment generally increased the Cd, Zn and Cu concentrations in crops but there was no consistent effect on the Ni, Pb and Cr concentrations. Buckwheat and Swiss chard exhibited the largest heavy metal concentrations followed by soybean and Romaine lettuce, and wheat and orchard grass. Wide variations in the organic matter contents and cation exchange capacities of soils exhibited little effect on the heavy metal concentrations in crops. However, decreasing soil pH increased the heavy metal concentrations in crops and this effect was very large for Cd, Zn and Cu in Swiss chard. Lime sludge treatment reduced the Cd concentration in Swiss chard and did not increase the Zn concentration relative to the commercial fertilizer treatment. Increasing the sludge application rate and discontinuing sludge application to soil had little effect on the heavy metal concentrations in crops.

INTRODUCTION

The effects of land application of sewage sludge on crop yield and quality and on groundwater quality have been studied at Environment Canada's Wastewater Technology Centre, Burlington. Field crops including orchard grass, wheat, buckwheat, and soybean, and vegetable crops including Swiss chard and Romaine lettuce have been grown in lysimeters. The purpose of this paper is to compare heavy metal concentrations in the crops and to consider the effects on these concentrations of several sludge and soil factors.

EXPERIMENTAL

Liquid Sludge Experiment

A lysimeter experiment in which orchard grass (Dactylis glomerata L.) cultivar Frode was grown on Conestoga loam and Caledon loamy sand soils (Table 1) receiving repeated surface applications of liquid sludges was initiated in 1973. The lysimeters were 30.5 cm diameter by 183 cm deep and the experiment consisted of three replicates of eleven fertility treatments arranged in a randomized block design. The fertility treatments included three rates of three sludges and two controls. Alum (Al), ferric chloride (Fe) and lime (Ca) treated sludges (Table 2) were applied at rates of 100, 200 and 300 kg N/ha and NPK fertilizer was applied to one of the control treatments. The other control treatment received neither sludge nor fertilizer. The sludge and fertilizer applications were made at the beginning of the growing season and following all but the last harvest of orchard grass each year. Potassium was applied to the sludge treatments to maintain optimum growth. Sludge and fertilizer were applied twenty-one times during 1973-1977 and the total sludge dry matter loadings at the 300 kg N/ha sludge application were 156, 158 and 390 tonnes/ha for the Al, Fe and Ca sludges, respectively. Further details of this experiment may be obtained from Webber et al (1981).

Following 1977, the experiment was modified. One block of treatments was replaced by a third soil, Brady fine sand, and the remaining treatments of Conestoga and Caledon soils were cultivated to a depth of 15 cm. Sludge application to the Conestoga soil was terminated. In the spring of 1978, orchard grass was planted on all three soils and sludge application to the Caledon soil was resumed with the same sludge types and rates as in 1977. In addition, Guelph sludge which exhibited a large Cd content (Table 2) was applied at 300 kg N/ha to Brady soil and to the treatment of Conestoga and Caledon soils that previously had received neither commercial fertilizer nor sludge.

NPK fertilizer was applied to a control treatment of each soil, N was applied to the previously sludged Conestoga soil and K was applied to all sludge treatments to maintain optimum growth.

TABLE 1. SOIL PROPERTIES (0-15 cm depth)

	pH	Organic Matter %	CEC* meq/100g
<u>Liquid Sludge Experiment</u>			
Brady fine sand	4.4	1.0	0.6
Caledon loamy sand	7.4	2.2	9.0
Conestoga loam	7.3	4.9	18.2
<u>Air-Dried Sludge Experiment</u>			
Plainfield Sand	5.6	2.1	4.7
New Liskeard Clay	7.2	6.4	28.2

*Cation exchange capacity

TABLE 2. TYPICAL SLUDGE PROPERTIES

	P Removal Chemical	pH	Solids	N	P	Cd	Zn	Cu	Ni	Pb	Cr
			-----g/L-----			-----mg/L-----					
Tillsonburg	Alum (Al)	7.6	39	1.8	1.4	3.4	403	71	5	60	88
North Toronto	Ferric chloride (Fe)	7.3	39	1.8	0.9	0.9	72	62	1	66	32
Midland	Lime (Ca)	6.7	38	0.7	2.3	0.3	247	24	92	27	133
Guelph	Alum	7.4	36	2.0	1.5	5.0	680	95	3	71	120

The experiment was modified again following 1979. Sludge application to all soils was terminated and they were cultivated to a depth of 15 cm. During 1980 one crop each of Swiss chard (Beta vulgaris var. cicla) cultivar Fordhook Giant and Romaine lettuce (Lactuca sativa) cultivar Paris Island Cos were grown. Commercial fertilizer was applied as required to maintain optimum growth.

Air-Dried Sludge

A Lysimeter experiment in which spring wheat (Triticum aestivum) cultivar Glenlea and buckwheat (Fagopyrum esculentum Moench) cultivar Tokyo were grown on Plainfield sand and New Liskeard clay (Table 1) receiving repeated applications of air-dried sludges was initiated in 1974. The lysimeters were 61 cm square by 76 cm deep and the experimental design was the same as for the liquid sludge experiment. The fertility treatments included three rates of air-dried Al, Fe and Ca sludges, incorporated into the surface 15 cm of soil, and two controls. One of the control treatments received NPK fertilizer and the other received neither sludge nor fertilizer. Potassium was applied to all sludge treatments to maintain optimum growth. The sludge and fertilizer treatments were repeated several times during 1974-1977 and the total N loadings at the three sludge application rates were 2328, 4656 and 6984 kg/ha, respectively. Total dry matter loadings at the 6984 kg N/ha sludge application rate were 276, 298 and 426 tonnes/ha for the Fe, Al and Ca sludges, respectively. Further details of this experiment may be obtained from Webber et al (1981).

The experiment was modified following 1977 when sludge application was discontinued. Crops of soybean (Glycine max (L.) Merr.) cultivar Harcourt were grown in 1978 and 1979 and of Swiss chard and Romaine lettuce were grown in 1980. Commercial fertilizer was applied as required to maintain optimum growth.

Soils

The soils used in both the liquid and air-dried sludge experiments (Table 1) were chosen to represent contrasting textures, organic matter contents and cation exchange capacities. Brady

fine sand was included in the liquid sludge experiment following 1977 to determine the effect of sludge application to an acid sandy soil with a very low organic matter content and cation exchange capacity. The Conestoga loam soil was obtained from the Guelph University, Experimental Farm and is the soil on which land application of sludge field experiments with corn and brome grass have been conducted.

Sludges

The Tillsonburg, North Toronto and Midland sludges (Table 2) were used in both the liquid and air-dried sludge experiments and represent the three different chemical treatments; alum (Al), ferric chloride (Fe) and lime (Ca), for phosphorus removal from wastewaters. Guelph sludge was used in the liquid sludge experiment following 1977. It exhibited a large Cd content and was applied to the Caledon, Conestoga and Brady soils to determine its effect on the growth and Cd concentrations in crops.

RESULTS

Crop Effects

Crop effects on heavy metal concentrations in plant materials are illustrated for spring wheat, buckwheat, soybean, Swiss chard and Romaine lettuce grown in the air-dried sludge experiment (Figure 1). The final sludge application to soils in this experiment was made prior to planting the wheat in 1977.

Relative to the other crops, buckwheat exhibited high concentrations of all heavy metals. Swiss Chard exhibited high concentrations of Cd, Zn, Cu and Cr and soybean exhibited high concentrations of Ni. Wheat grain exhibited smaller Cd, Ni and Pb concentrations than wheat straw. Soybean grain exhibited smaller Cd, Pb and Cr concentrations and larger Ni concentrations than soybean vegetation. These differences were observed for both the commercial fertilizer and sludge treatments. In general, sludge treatment increased the Cd and Zn concentrations and slightly increased the Cu concentrations in plant materials. There was no consistent effect of sludge treatment on the Ni, Pb and Cr concentrations.

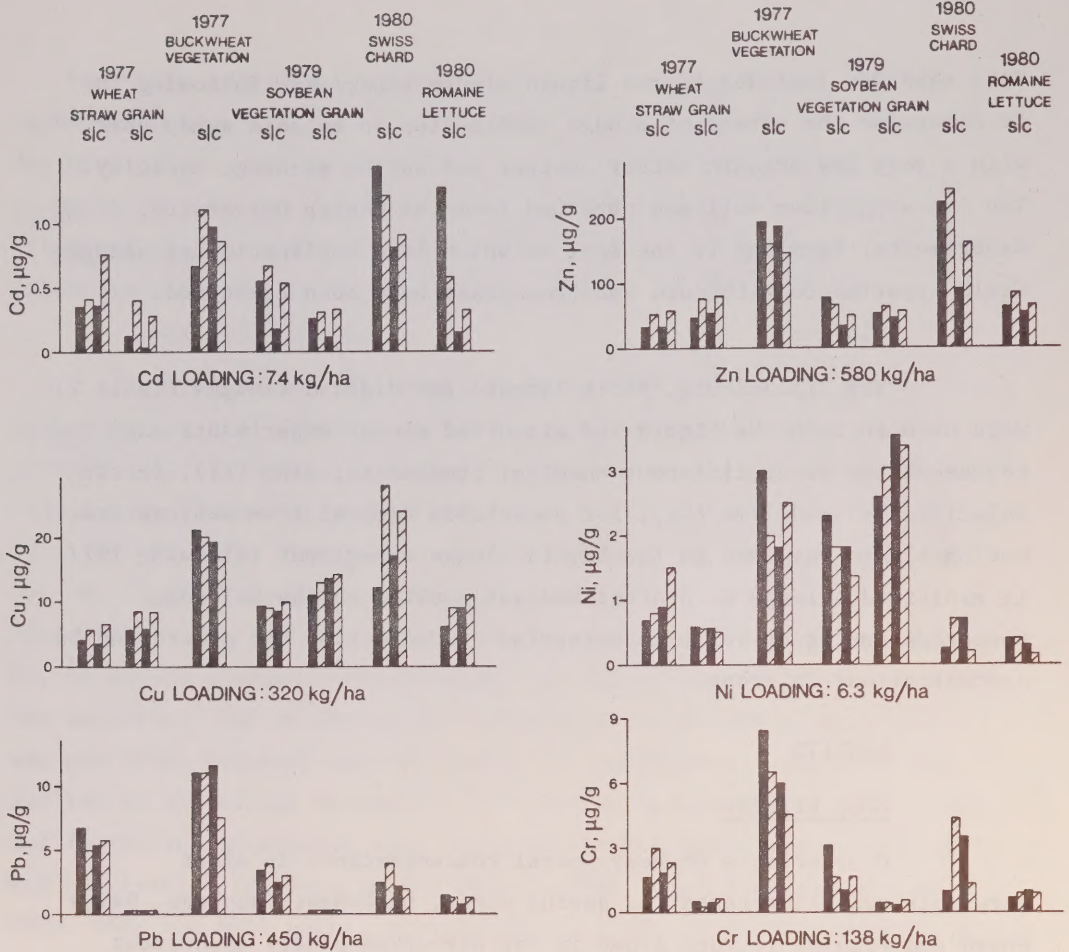


FIGURE 1. METAL CONCENTRATIONS IN CROPS GROWN ON PLAINFIELD SAND (S) AND NEW LISKEARD CLAY (C) TREATED WITH COMMERCIAL FERTILIZER (SOLID BAR) AND AIR-DRIED Fe SLUDGE (HATCHED BAR)

With few exceptions the heavy metal concentrations in plant materials grown on Plainfield sand and New Liskeard clay were similar. Swiss chard and Romaine lettuce grown on the commercial fertilizer treatment of Plainfield sand exhibited larger Cd concentrations than when grown on the sludge treatments. This observation is probably related to soil pH. For many crops Cd uptake increases as soil pH decreases. In 1980, the pH of Plainfield sand treated with commercial fertilizer was 5.2 and with Fe sludge was 6.4.

A comparison of orchard grass, Swiss chard and Romaine lettuce grown on the liquid sludge experiment is presented in Figure 2. In general, orchard grass exhibited smaller concentrations of Cd, Zn and Cu and equal or slightly larger concentrations of Ni, Pb and Cr than chard and lettuce. Guelph sludge treatment caused large increases in the Cd and Zn concentrations of these crops, small increases in Cu concentrations and inconsistent effects on the Ni, Pb and Cr concentrations.

Soil Effects

The Conestoga, Caledon and Brady soils employed in the liquid sludge experiment were chosen to represent marked contrasts of texture, pH, organic matter content and cation exchange capacity (Table 1).

Cadmium, Zn and Ni concentrations in crops grown on the Conestoga and Caledon soils were similar and generally smaller than in crops grown on Brady soil (Figure 2). However, there was no consistent effect of soil type on the Cu, Pb and Cr concentrations in crops. Soil acidity affected crop growth on the Brady soil and Romaine lettuce did not survive on the commercial fertilizer treatment. One replicate of Swiss chard survived but did not grow well and exhibited larger Ni and Cr concentrations than for the sludge treatment. Guelph sludge treatment increased the pH of Brady soil from 4.4 to 6.1.

Effects of Sludge Type

Three types of sludge resulting from the addition of alum (Al), ferric chloride (Fe) and lime (Ca) to remove phosphorus from wastewaters were applied to soils in the liquid sludge experiment. Heavy metal loadings to the soils were generally large, however, they varied with sludge type (Figure 3).

With few exceptions, the heavy metal concentrations in orchard grass and Romaine lettuce exhibited no consistent variation with sludge type. There was no effect on the Cd, Cu, Pb and Cr concentrations of these crops. Zinc concentrations were marginally

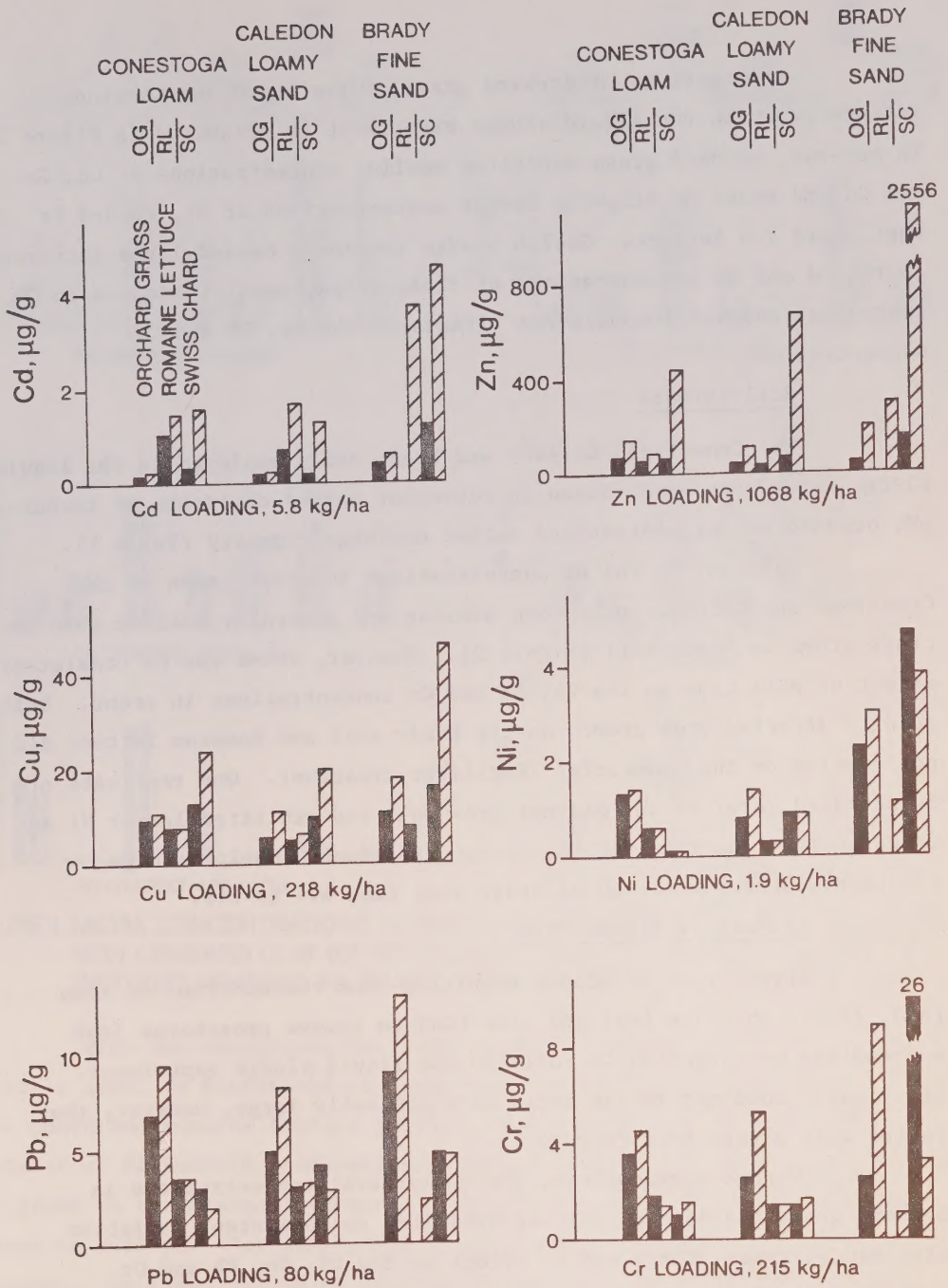


FIGURE 2. METAL CONCENTRATIONS IN CROPS GROWN ON THREE SOILS TREATED WITH COMMERCIAL FERTILIZER (SOLID BARS) AND LIQUID GUELPH SLUDGE (HATCHED BARS)

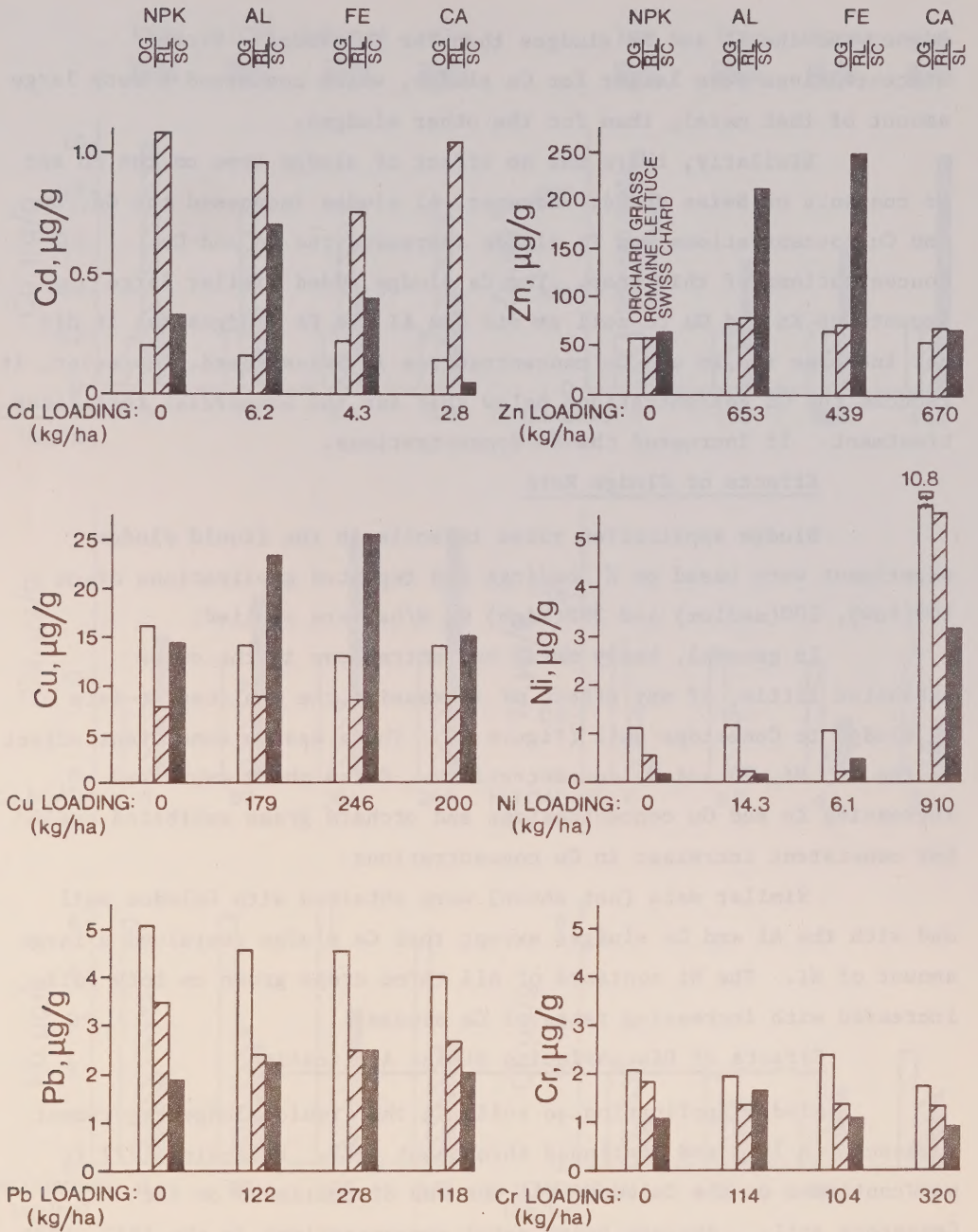


FIGURE 3. METAL CONCENTRATIONS IN CROPS GROWN ON CONESTOGA LOAM TREATED WITH COMMERCIAL FERTILIZER AND LIQUID AL, Fe AND Ca SLUDGES

higher for the Al and Fe sludges than for Ca sludge. Nickel concentrations were larger for Ca sludge, which contained a very large amount of that metal, than for the other sludges.

Similarly, there was no effect of sludge type on the Pb and Cr contents of Swiss chard. However, Al sludge increased the Cd, Zn and Cu concentrations and Fe sludge increased the Zn and Cu concentrations of this crop. The Ca sludge added similar large amounts of Zn and Cu to soil as did the Al and Fe sludges but it did not increase the Zn and Cu concentrations in Swiss chard. Moreover, it reduced the Cd concentrations below that for the commercial fertilizer treatment. It increased the Ni concentrations.

Effects of Sludge Rate

Sludge application rates to soils in the liquid sludge experiment were based on N loadings and repeated applications of 100(low), 200(medium) and 300(high) kg N/ha were applied.

In general, heavy metal concentrations in the crops exhibited little, if any effect of increasing the application rate of Fe sludge to Conestoga soil (Figure 4). There was no consistent effect on the Cd, Ni, Pb and Cr concentrations. Swiss chard exhibited increasing Zn and Cu concentrations and orchard grass exhibited small but consistent increases in Cu concentrations.

Similar data (not shown) were obtained with Caledon soil and with the Al and Ca sludges except that Ca sludge contained a large amount of Ni. The Ni contents of all three crops grown on both soils increased with increasing rates of Ca sludge.

Effects of Discontinuing Sludge Application

Sludge application to soils in the liquid sludge experiment commenced in 1973 and continued throughout 1977. Following 1977 it was continued on the Caledon soil but was discontinued on the Conestoga soil. Average heavy metal concentrations in the 1977, 1978, and 1979 orchard grass grown on these soils are presented in Figure 5.

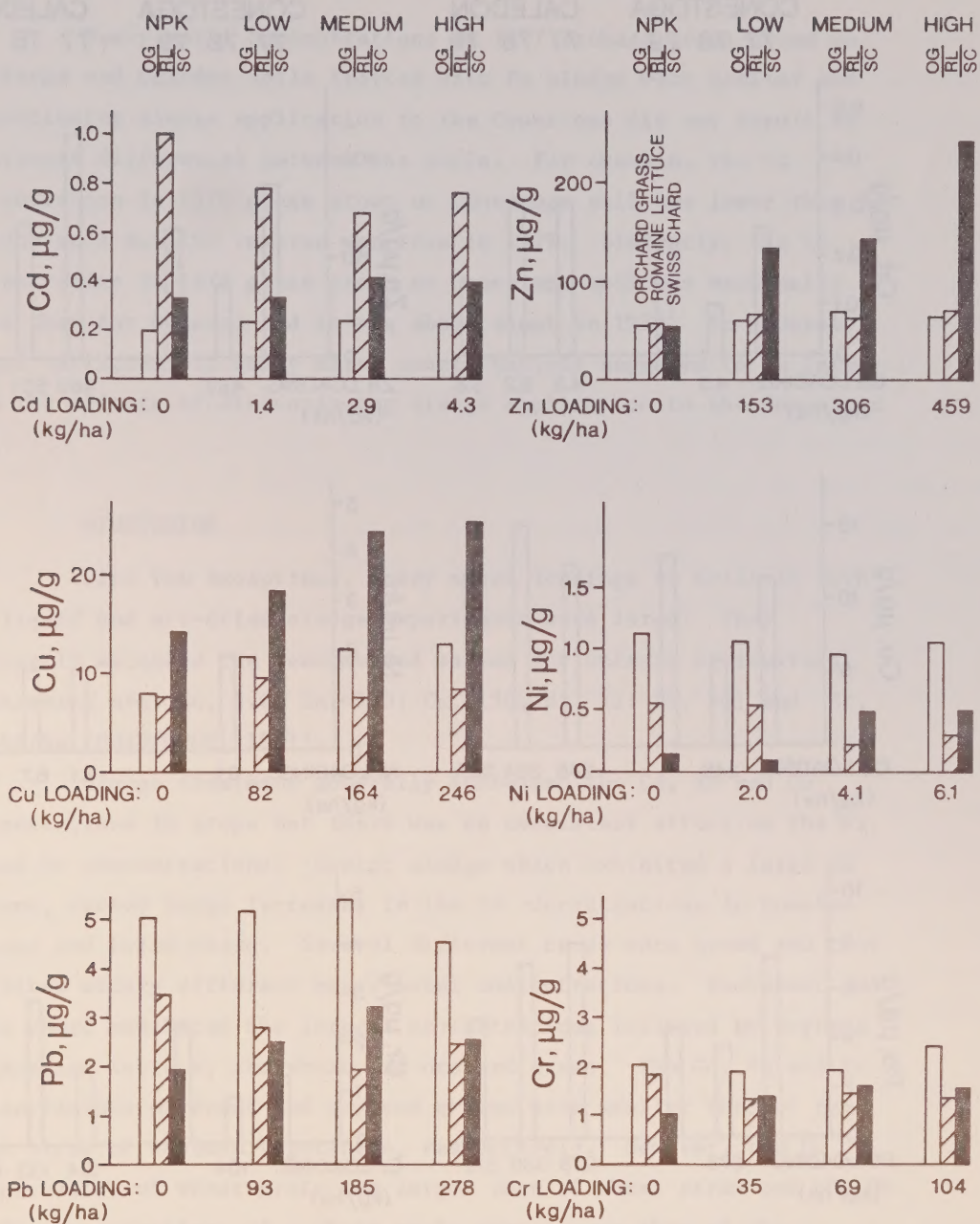


FIGURE 4. METAL CONCENTRATIONS IN CROPS GROWN ON CONESTOGA LOAM TREATED WITH COMMERCIAL FERTILIZER AND THREE RATES OF LIQUID Fe SLUDGE

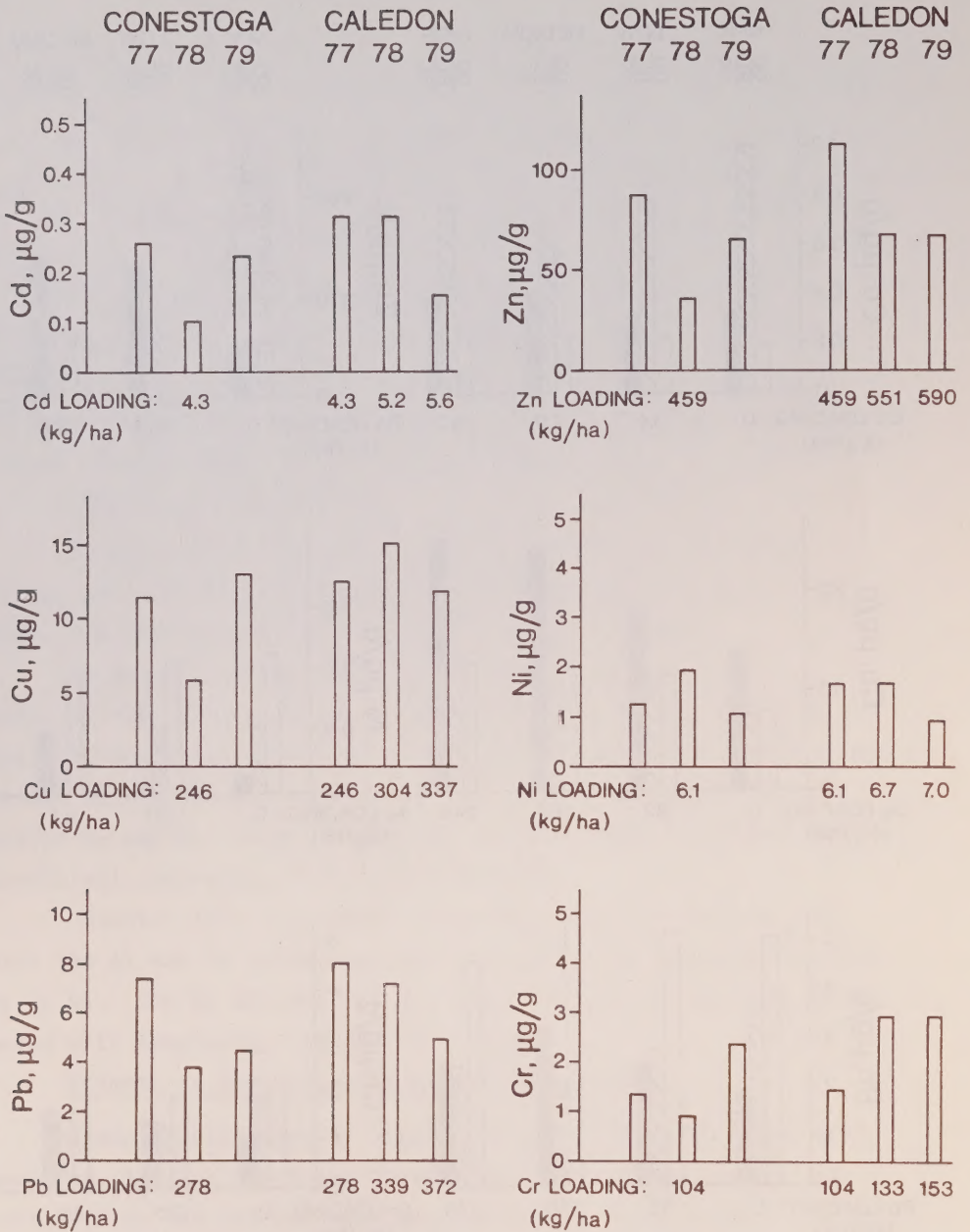


FIGURE 5. METAL CONCENTRATIONS IN ORCHARD GRASS GROWN ON CONESTOGA SOIL ON WHICH LIQUID Fe SLUDGE APPLICATION WAS DISCONTINUED AFTER 1977 AND ON CALEDON SOIL ON WHICH IT WAS CONTINUED AFTER 1977

Heavy metal concentrations in 1977 orchard grass grown on Conestoga and Caledon soils treated with Fe sludge were similar and discontinuing sludge application to the Conestoga did not result in consistent differences between the soils. For example, the Cd concentration in 1978 grass grown on Conestoga soil was lower than for Caledon soil but the reverse was true in 1979. Similarly, the Zn concentration in 1978 grass grown on Conestoga soil was marginally lower than for Caledon and it was about equal in 1979. In general, annual variations in heavy metal concentrations appeared to be larger than the effects of discontinuing sludge application to the Conestoga soil.

DISCUSSION

With few exceptions, heavy metal loadings to soils in both the liquid and air-dried sludge experiments were large. They frequently exceeded the recommended maxima for Ontario Agricultural lands which are: Cd, 1.6; Zn, 330; Cu, 150; Ni, 32; Pb, 90; and Cr, 210 kg/ha (OMAF/OMOE, 1981).

Sludge treatment generally increased the Cd, Zn and Cu concentrations in crops but there was no consistent effect on the Ni, Pb and Cr concentrations. Guelph sludge which exhibited a large Cd content, caused large increases in the Cd concentrations in Romaine lettuce and Swiss chard. Several different crops were grown and they exhibited widely different heavy metal concentrations. Buckwheat and Swiss chard exhibited the largest concentrations followed by soybean and Romaine lettuce, and wheat and orchard grass. The Cd, Pb and Cr concentrations of wheat and soybean grains were smaller than of the wheat straw or soybean vegetation, respectively. However, the Cu concentration of wheat grain was larger than of wheat straw and the Cu and Ni concentrations of soybean grain were larger than of the vegetation. Differences in heavy metal concentrations between crop species and plant parts are well documented (CAST Committee Report,

1976). Usually, leafy vegetables exhibit larger concentrations than most other crops and roots, leaves and stems exhibit larger concentrations than the reproductive parts.

Wide variations of organic matter content and cation exchange capacity in soils exhibited little effect on heavy metal concentrations in crops. Crops grown on the Caledon, Conestoga and New Liskeard soils (Table 1) showed similar heavy metal concentrations. Decreasing soil pH increased the heavy metal concentrations in crops and this effect was large for the strongly acid Brady soil (pH 4.4) and for Swiss chard. Swiss chard grown on sludge treated Brady soil exhibited very large increases in Cd, Zn and Cu concentrations. Metal concentrations in crops grown on Plainfield soil (pH 5.6) were similar to those in crops grown on the Caledon, Conestoga and New Liskeard soils with pH 7. These observations support the view that pH is the most critical soil factor relative to Cd and Zn uptake by crops and that a decrease from 6 to 5 will likely result in greater increases in uptake by crops than a decrease from 7 to 6 (CAST Committee Report 1981).

The effects of sludge type on metal concentrations in crops were confounded with the effects of metal loadings. The metal loading varied with sludge type. However, it was apparent that Ca sludge exhibited different effects than the Al and Fe sludges particularly with Swiss chard. A reduction of Cd concentration and no increase in the Zn concentration of Swiss chard relative to the commercial fertilizer treatment was probably caused by the large amount of calcium carbonate contained in the Ca sludge.

In general, there was little effect on heavy metal concentrations in crops of increasing the sludge application rate or of discontinuing sludge application to soil.

ACKNOWLEDGMENTS

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GAS PRODUCTION AND MIGRATION
AT CLOSED LANDFILLS IN ONTARIO

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INTRODUCTION

In recent years, considerable work has been undertaken in Canada and the United States to determine the suitability of sanitary landfill sites as a source of methane gas for heating purposes. In Ontario, pilot methane extraction projects have been conducted at St. Thomas (Conestoga Rovers, 1979), and are planned for the Beare Road landfill in Toronto. In contrast to the possible benefits of methane generation from landfills, is the potential hazard of methane migrating to adjacent land areas. The latter has become a concern in many municipalities as a result of urban expansion into areas formerly used for the disposal of municipal wastes.

The current study is being undertaken by Hydrology Consultants to assist the Ontario Ministry of the Environment in preparing guidelines for land development adjacent to landfill sites in Ontario. Included in this study is a comprehensive state-of-the-art review of literature dealing with methane

production and migration; evaluation of site assessment procedures including installation of test probes, methane detection equipment, sampling, and analytical techniques; the determination of the rate and extent of methane migration under various geologic conditions; and the effectiveness of various types of control systems. This paper, however, will deal only with the results of the gas migration study and associated monitoring procedures.

STUDY AREAS

Ten sites were chosen across Ontario as being representative of closed sanitary landfills in various geologic environments. For comparative purposes three "inert" and seven controlled sites were chosen. The "inert" or clean fill sites had reportedly been used for disposal of fly-ash from power stations, or construction materials. The controlled landfills are those where systems of various designs had been installed to restrict off-site migration of methane.

REPRESENTATIVE LANDFILLS

Barrie - Sandy Hollow

The Sandy Hollow landfill has an area of approximately 22 hectares and is located on the flank of an upland area near the western boundary of the municipality. Overburden consists of 150 m+ of glaciolacustrine sands, of which the upper 75 m lies above the water table. The potential for methane migration to the south of the site is reduced by the presence of a deep ravine which functions as a cut-off trench. To the north, a 75 m thickness of unsaturated sand greatly increases the potential for migration.

Over the last 13 years, the landfill has received a variety of domestic, commercial and industrial wastes. The site will remain open for about another six years.

Kitchener - Ottawa Street

The Ottawa Street landfill in Kitchener has an area of about 30 hectares and has been built to a height of 30 m above the surrounding till plain. The site was active for about 20 years before closing in 1978. An active venting system has been installed along the northeast boundary to control migration of methane.

Niagara Falls - Victoria Avenue

The Victoria Avenue landfill in Niagara Falls has an area of about 6 hectares, and occupies a small valley cut in stratified sands, silts, and clays which overlie the dolomite limestone bedrock to a depth of 15m+. Initial fill at the site consisted of ashes, cinders and incinerated municipal refuse. During the final years of operation (1959-62) domestic wastes were buried without incineration.

Ottawa - Riverside Drive

The Riverside Drive landfill in Ottawa covers an area of about 30 hectares on the flood plain of the Rideau River. The site is underlain by alluvial deposits, primarily sandy silt. During the period 1954 to 1957, the site received approximately 6 m of fill consisting of domestic and industrial wastes. To the east of the site, a thin and variable thickness of overburden covers the bedrock. The Rideau River forms an effective barrier to methane migration along the western boundary of the site.

Owen Sound - Ninth Avenue East

This landfill has an area of about 6 hectares, and is located in a former quarry on Ninth Avenue East, north of Highway 26. The site received domestic refuse from the city until 1970 when it was filled to the grade of the original surface. The overburden consists of a clayey till, usually less than 0.5 m in thickness, that overlies dolomite limestone.

Waterloo - Erb Street

The Erb Street landfill covers 14 hectares near the western boundary of the municipality in an area of silty to clayey till that overlies a considerable thickness of fine to coarse grained kame sand. To the west of the site, the fill is absent, and high water table conditions form an effective barrier to possible gas migration. A 300 m wide Hydro corridor provides an effective buffer zone along the eastern boundary of the landfill. The site is active and currently has an accumulation of about 15 m of domestic refuse and sand.

THEORY OF GAS PRODUCTION

Under anaerobic (oxygen deficient) conditions such as occur in landfills, complex organic wastes such as sewage sludge, food, paper, wood and garden materials can be biologically converted to methane and carbon dioxide. The process of conversion to methane is complex but essentially consists of two stages -

- (1) formation of acetic acid and propionic acid by facultative and anaerobic bacteria.
- (2) formation of methane and carbon dioxide from acetic and propionic acid by strictly anaerobic methanogenic bacteria.

Optimum production of methane occurs when soil/soil water pH = 7, and bicarbonate alkalinity is greater than 500 mg/l (Emcom Associates, 1980). Work by Chian and DeWalle (1977) and Rovers (1972) indicated that the pH of young landfills tended to be 6 or lower (organic acid phase) and approached 7 after 10 to 15 years.

Methane may be produced in landfills where mean pH is less than 6. In these cases, the methane is probably being produced in oxygen free micro-environments in the landfill where the pH and alkalinity are within the optimum range.

Methane is explosive in concentrations between 5 and 15 percent by volume in air.

THEORY OF GAS MOVEMENT

Methane gas migrates in response to differentials of concentration (diffusion), and pressure (convective movement). A third mechanism of flow, dispersion, was shown by Mohsen et al (1978) to be insignificant at the flow velocities expected in soil.

The basic equation for gas movement through porous media (soil) is:

$$F_x = D_x \frac{\partial c}{\partial x} - \frac{K}{\mu} \frac{\partial p}{\partial x}$$

where F_x = flow through a unit effective area of porous medium perpendicular to the flow direction

D_x = coefficient of diffusion

$\partial c / \partial x$ = concentration gradient in flow direction

K = intrinsic permeability of porous medium

μ = viscosity of gas mixture

$\partial p / \partial x$ = pressure gradient in flow direction

Movement due to diffusion is dependent on the coefficient of diffusion for the medium. Studies by the County of Los Angeles and Engineering Science Inc. (1969), and Farquhar et al (1980), showed that the rates of diffusion in fine grained soils are considerably slower than in coarse grained soils. The County of Los Angeles study reported diffusion coefficients from .026 m²/sec. for silty clay to 1.34 cm²/sec. for gravel. Dry kaolin clay was found to form an almost total barrier to gas migration.

Convective movement of methane is associated with pressure gradients between landfill and surrounding materials, and may be several orders of magnitude greater than movement by diffusion. In the landfills studied during the current program, significant but low pressure differences (less than 0.5 kPa) were measured on-site. Extention of pressure gradients

off-site has not been possible up to now. Work by Farquhar et al (1980) found that under static conditions atmospheric and internal landfill pressures did not differ by more than 0.3 kPa. Frequent reversals of the pressure gradient were observed into and out of the landfill. Time lags up to 100 min occurred between barometric change and response of landfill pressures. Similar findings were reported by Moore and McOmber (1981) in studies of landfills at Lees Lane, Kentucky, and Mississauga, Ontario.

FIELD PROGRAM

In order to obtain data on methane gas concentrations and migration at landfills, gas probes were installed on site and off site. The standard installation procedure involved augering a 180 mm hole to the desired depth and installing a length of 13 mm diameter O.D. slotted polyethylene tubing. The hole was then backfilled with sand and sealed near the surface with bentonite concrete. When information was required at several levels in the landfills, multiple probes were installed and isolated with bentonite seals.

Field measurements in the probes consisted of probe pressure, temperature at various depths, groundwater levels, and methane concentrations. Methane concentrations were determined by portable gas detector.

In order to determine the concentration of oxygen, carbon dioxide and nitrogen and to verify the concentration of methane, samples of probe gas were collected in 50 cc plastic syringes. The samples were later analyzed in the laboratory by gas chromatograph.

Several other types of gas sampling container are currently being evaluated. These include metal containers, glass syringes, gas bottles and teflon bags. Factors being considered are - ease of sample collection, storage life of the gas samples and durability. Our preliminary evaluation shows that the 50 cc plastic syringes are satisfactory for sample storage up to one week (see also Emcom, 1981, p. 72).

EXTENT OF METHANE MIGRATION

Methane being lighter than air will tend to vent vertically through a landfill cover to the atmosphere, although differential permeabilities within a landfill and adjacent materials may cause some lateral migration of gas. Service trenches lined with coarse granular materials, adjacent to or within landfills, provide possible routes for lateral migration.

The greatest potential for lateral migration of methane gas occurs during the winter months when the formation of a frost layer on the landfill surface prevents natural venting of methane. Concentration (diffusion) and pressure (convection) gradients between the landfill and adjacent areas create the conditions for lateral migration.

In the present study, the maximum extent of migration was considered to be detection of a methane concentration of 0.1 percent (1000 ppm) by volume in off-site monitoring probes. This value represents the lower limit of measurement for commonly used portable gas detection instruments. There are some portable instruments available that can detect methane in concentrations as low as 10 ppm, but these are not widely used.

In the current study, the maximum observed migration of methane from a landfill, was about 150 m. This occurred at the Sandy Hollow landfill site near Barrie, Ontario during the winter. As noted earlier, this site is flanked to the north by unsaturated sands; a condition conducive to methane migration particularly during the winter when vertical venting of the gas through the landfill is restricted.

In areas where the landfill is bounded by bedrock, the extent of methane migration depends on the nature of the rock and the degree of fracturing. At the Victoria Avenue site in Niagara Falls, no off-site migration of methane was observed into the surrounding dolomitic limestone. At the Owen Sound site on Ninth Avenue East, some off site migration was observed, but was less than 30 m. The migration probably occurred through minor fracturing in the limestone bedrock, or through a pocket of sand that was used as a ramp to the former quarry.

At locations where saturated conditions exist in materials adjacent to the landfill, such as on the west side of the Erb Street site at Waterloo, off site migration of methane was not observed.

Off site migration was generally minimal at sites in areas of clay or those protected by fan aspirated control systems, such as exist at the Ottawa Street landfill in Kitchener.

CONCLUSIONS

The extent of lateral migration of methane gas from landfills depends on a number of factors, including: pressure (convective) and diffusion (concentration) gradients between a landfill and adjacent materials, permeability of surrounding materials, and seasonal climate.

The maximum extent of off-site migration observed during the current study was 150 m. This occurred during the winter at a site surrounded by unsaturated coarse granular materials. Off-site migration was generally minimal in areas of clay or those protected by an active control system.

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CONTAMINANT OCCURRENCES IN UNCONFINED SAND AQUIFERS
AT TWO MUNICIPAL LANDFILLS

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S.A. Abdul¹, E.J. Reardon¹, and C.I. Mayfield²

Abstract

This paper describes the on-going investigations of the occurrence and migration of contaminants in permeable sand aquifers at two municipal landfills. These are located near Elmira in the Regional Municipality of Waterloo (Woolwich site) and near the City of North Bay (North Bay site). Both lie on bedded glacio-fluvial sand deposits. A network of multilevel sampling devices is being used to obtain a three-dimensional delineation of the plume of contamination in the sand aquifer at each site.

Studies at the North Bay site are emphasized. The maximum extent of the plume was initially identified using chloride and electrical conductance. Concentrations of iron, sodium, manganese, zinc, major cations, ammonium, organic nitrogen, inorganic carbon and organic carbon are considerably above background throughout the plume. Many of these constituents have the same general trends in concentration patterns as chloride. None of the toxic metals listed in drinking water standards have migrated from beneath the landfill. The plume extends a distance of 750 m to a large iron-stained discharge area where springs feed a small stream that flows through the City of North Bay. Leachate springs also occur along the southern edge of the landfill and along the edge of a sand quarry about 200 m from the landfill. In spite of the unsightly occurrence of leachate springs and extensive discharge of iron-rich water, the influence of inorganic contaminants from the landfill on the quality surface water in the drainage basin is insignificant. Of greater potential importance are the organic compounds in the contaminated groundwater. Identification of these compounds, assessment of the toxicity of the groundwater in the plume, and carbon transformation studies using carbon isotopes and identification of specific organic compounds along the plume are the current areas of research focus.

Introduction

Of the various problems associated with the disposal of municipal waste by landfilling, the most serious long-term problem is the degradation of groundwater quality. In some situations contamination by landfill leachate causes water supply wells to become unuseable, or at sites where the groundwater zone is not used as a water supply, landfill-derived contaminants may migrate through the groundwater zone and adversely affect the water quality in streams, marshes or lakes. In more favorable hydrogeological circumstances, the leachate-derived constituents may enter the groundwater zone and undergo a sufficient degree of attenuation to prevent

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significant adverse effects on water resources.

Tens of thousands of major dumps and landfills exist in North America and because landfilling continues to be the fate of most refuse, hundreds of new sanitary landfills are established each year. A major problem now facing hydrogeologists and environmental engineers is the selection of new landfill sites that will not result in excessive degradation of groundwater quality and the identification of old sites where problems may arise in future years. The prediction of the migration and attenuation of landfill-derived constituents in the groundwater zone is an inherent part of these tasks.

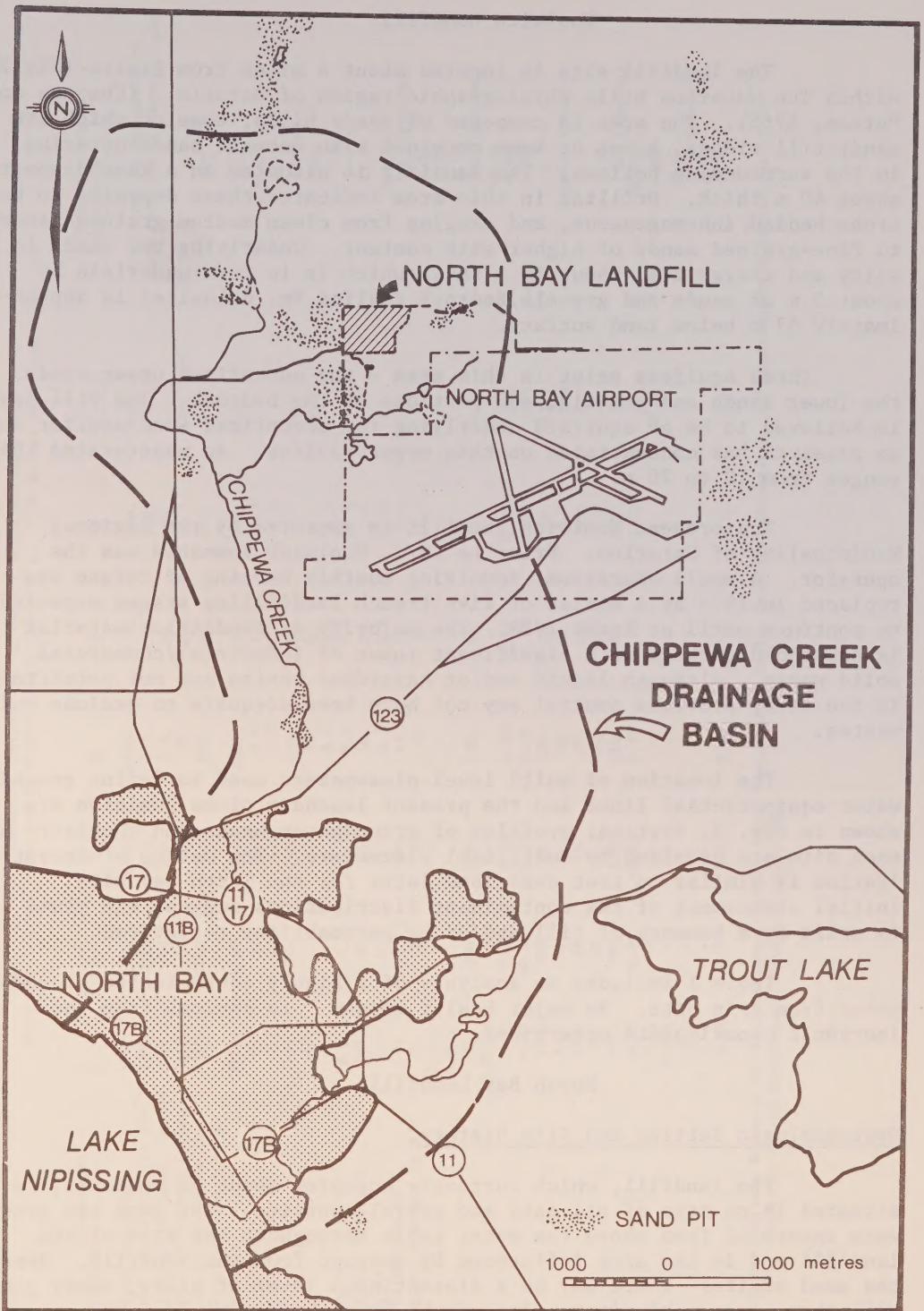
Since the mid 1970's, the hydrogeology group at the University of Waterloo has been engaged in research activities designed to provide an improved understanding of the behavior of landfill-derived contaminants in groundwater. A major component of this research effort involves detailed field studies of abandoned or existing landfills situated on permeable geological deposits. New methods of monitoring are being developed and the processes of dispersion and geochemical and biogeochemical attenuation of contaminants are being investigated.

At the present time plumes of contaminated groundwater at five landfills situated on unconfined sand aquifers are being studied. This paper describes some of the preliminary results obtained from two of these sites, the North Bay landfill, located on the precambrian Shield near the City of North Bay in north-central Ontario (Fig. 1), and the Woolwich landfill, located in southern Ontario in the Regional Municipality of Waterloo (Woolwich Twp.) (Fig. 2).

Research at the Woolwich site is preliminary and will be discussed very briefly. This site was chosen because of the thick (20-30 m) unsaturated zone at the site, in contrast to the generally less than 10 m depth to water table at the North Bay site. A contrast in thick and thin unsaturated zones was desired because of the potential effects on inorganic, organic and gaseous solute transport in the unsaturated zone. The North Bay site was selected because it was known from previous investigations by consultants to have a contaminant plume of considerable size and because it is located on deposits that have no significant content of carbonate minerals. The other landfills that we are investigating are situated in southern Ontario where the aquifers have abundant carbonate-mineral content. The results of investigations of one of these landfills are described in a series of papers by MacFarlane et al. (1981), Cherry et al. (1981) and others. A contrast in carbonate-mineral content was desired because in some hydrogeochemical settings carbonate minerals can exert an important influence on the geochemical system and in particular on the pH and related metal-solubility relationships.

The purpose of this paper is to present a description of the initial results obtained at these two sites. The emphasis during this period has been on defining the hydrogeology and on delineating the zone of contaminated groundwater and the distribution of various inorganic contaminants within it. In the on-going phase of the investigation, the contaminant distributions are being determined in more detail, the hydrogeochemical controls and the effect of dispersion on various inorganic elements in the contaminated zone are being evaluated and the occurrence, toxicity, adsorption and biochemical transformation of organic compounds are being studied.

Figure 1. Geographic settings of the North Bay landfill



In some areas, the sand has a beach or near-shore glacial lake origin.

The landfill is situated on the edge of a spruce bog that drains via small channels with intermittent flow into Chippewa Creek, which flows through the City of North Bay into Lake Nipissing (Fig. 1). Except during the period of spring runoff, the flow in Chippewa Creek in the area southwest of the landfill is a few tenths of a cubic metre per second or less.

Since its beginning in 1962, the site has not been operated in a manner that fits the formal description of a sanitary landfill. Although burial in cells with daily cover of earth material was sometimes practiced, most of the waste in the landfill was dumped, with little compaction and irregular and infrequent cover. The landfill has received domestic, commercial, solid industrial and small quantities of liquid industrial waste from the City of North Bay (population 50,000) and the neighboring townships. During the past few years dewatered sludge from the sewage treatment plant in the City of North Bay has been deposited regularly on top of the completed segments of the landfill. According to current plans, use of the landfill will be greatly reduced in the next few years as an energy recovery plant is put into operation.

Almost all of the refuse in the landfill is above the water table, which is within a metre or less of the bottom of the refuse beneath much of the landfill. The average annual precipitation in the North Bay area is 80 cm. The surface of the landfill is flat and the cover material, which is mostly sand, sawdust, or sludge, is permeable. Most of the rain and snow that falls on the landfill surface therefore infiltrates into the refuse.

Methods of Investigation

On various occasions since November, 1979, groundwater monitoring devices have been installed in the sand aquifer beneath the landfill and in the areas of apparent contaminant migration beyond the landfill. The groundwater monitoring network as it currently exists is shown in Fig. 4. The purpose of the monitoring network is to provide a means of delineating the areal and vertical distribution of landfill-derived contaminants in the sand aquifer. This delineation is being accomplished through an iterative procedure that involves several stages of drilling and the installation of monitoring devices.

Each stage involves about a week of drilling with a truck-mounted or tracked vehicle-mounted drill with hollow-stem augers. After the monitoring devices are installed during a particular stage, the devices are left for a period of time so that the disturbance of the groundwater zone around each device caused by drilling diminishes. Then, the devices are pumped to further remove water from the disturbed zone and subsequently they are monitored for water levels and sampled for analyses of electrical conductance or chloride. These data are then used to identify areas where the data base is inadequate and a subsequent phase of drilling and sampling is designed. By staging the installation of the groundwater monitoring network in this manner, the end result after several stages should be a network that has monitoring devices at all

Figure 2. Location of the Woolwich landfill



or nearly all of the locations necessary to define the extent of the plume and internal characteristics of the plume. It is expected that a minimum number of devices will exist at non-essential locations. The monitoring network that is now in place at the North Bay site is not complete, but it probably has at least three-quarters of the devices that will exist when the network is completed in 1982.

The monitoring devices that are being used in the North Bay investigation are bundle piezometers. They are described in detail by Cherry et al. (1981). A bundle piezometer consists of a bundle of nine 3/8 inch diameter polyethylene tubes bundled by tape around a 1/2 inch ID schedule 80 PVC pipe that serves as a semi-rigid centre piece and as the deepest piezometer in the bundle. Each polyethylene tube has a 10 cm long tip on the end. The tip is formed of nylon screen wrapped around the 10 cm length of perforated polyethylene tubing. Several larger diameter standpipe piezometers were also installed in the aquifer, primarily for response tests for hydraulic conductivity. Minature piezometers were installed by hand to depths of a metre or less in the wetland along the southern edge of the landfill. These devices are described by Lee and Cherry (1979).

At nearly all locations at the North Bay site, groundwater levels are within suction depth so that water sampling is conveniently accomplished using hand-operated vacuum pumps. At the few sites where water levels are deeper, water samples are obtained using a narrow-diameter tube with a one-way valve on the bottom as a bailer or using a nitrogen-gas Lift system (Robin and Gillham, in prep.) Water levels are measured using an electric probe.

At the North Bay site and at the other landfills on sand aquifers that we are investigating, electrical conductance and chloride are convenient parameters for the identification of groundwater with landfill-derived contaminants because these parameters are high in the leachate and very low in the natural groundwater. Small volume samples from each of the tubes in all of the bundle piezometers were collected in the summer of 1980 and 1981 for analysis of chloride and electrical conductance. The results of these analyses were used for preliminary mapping of the contaminant plume and based on this, large volume samples were obtained from between two and five sampling tubes at most monitoring sites. These samples were filtered in the field and analysed for major ions, a suite of metals, and trace-level non-metals such as arsenic and selenium, and for nitrogen species, alkalinity, and dissolved organic carbon. Measurements of pH, alkalinity and Eh (platinum electrode) were made on separate samples immediately after water was drawn from the aquifer.

Preliminary trace organic analyses have been carried out on five samples collected along the centre of mass of the plume. Most laboratory analyses have been performed by M.O.E., Toronto Laboratories.

Results

Geology and Groundwater Flow

There are two important trends in the slope of the water table in the vicinity of the landfill. Along the southern edge of the landfill, the water table slopes southward across the wetland adjacent to the landfill and into the spruce bog beyond. From the southwestern corner of the landfill the water table slopes to the southwest (Fig. 5). This dominant southwestward slope extends along the sand aquifer for a distance of about 750 metres to an area of groundwater discharge that feeds small tributaries to Chippewa Creek. These two main directions in the water table slope represent the directions of movement of contaminated groundwater that emanates from beneath the landfill.

The depth to the water table in the sand varies from a few metres near the landfill to less than a metre or two in the broad falt-bottomed sand pit southwestward of the landfill. Farther to the southwest, the land surface rises abruptly at the edge of the pit and beyond this point the water table is 15 to 20 metres below the plateau formed by the natural ground surface. Towards Chippewa Creek the land surface declines and the depth to water table becomes progressively shallower. The water table is at ground surface in the area characterized by springs and seepage zones that feed a small tributary to Chippewa Creek. The topography of the ground surface, the water table and approximate thickness of the aquifer along a southwestward trending cross section are shown on Figure 6.

The sand aquifer is underlain by a layer of silty sandy till that has a much lower hydraulic conductivity than the aquifer. Flow in the aquifer is therefore primarily horizontal and follows the southwestward slope of the water table. Estimates of the average groundwater velocity obtained using the Darcy equation are between approximately 50 and 200m/ year. The velocity is probably quite variable locally because the aquifer is heterogeneous.

Distribution of Contaminated Groundwater

Two zones of groundwater contaminated by chloride, organic compounds, and other constituents from the landfill, exist in the sand aquifer. The largest zone, hereafter referred to as the plume, extends to the area of springs and seeps that feed the tributary to Chippewa Creek (Fig. 7). This represents a linear travel distance of approximately 750 m. The plume of contaminated groundwater is narrow relative to the size of the landfill and it appears to follow a slight trough in the bedrock surface where the aquifer is most permeable.

The second zone exists beneath the wetland along the southern edge of the landfill. This zone, which occurs in a groundwater discharge area, is generally limited to within about 50 to 100 m of the landfill. It does not extend farther because nearly all of the flow from beneath the landfill moves upward to the surface within this area.

Figure 5. Contour map of the water table at the North Bay landfill

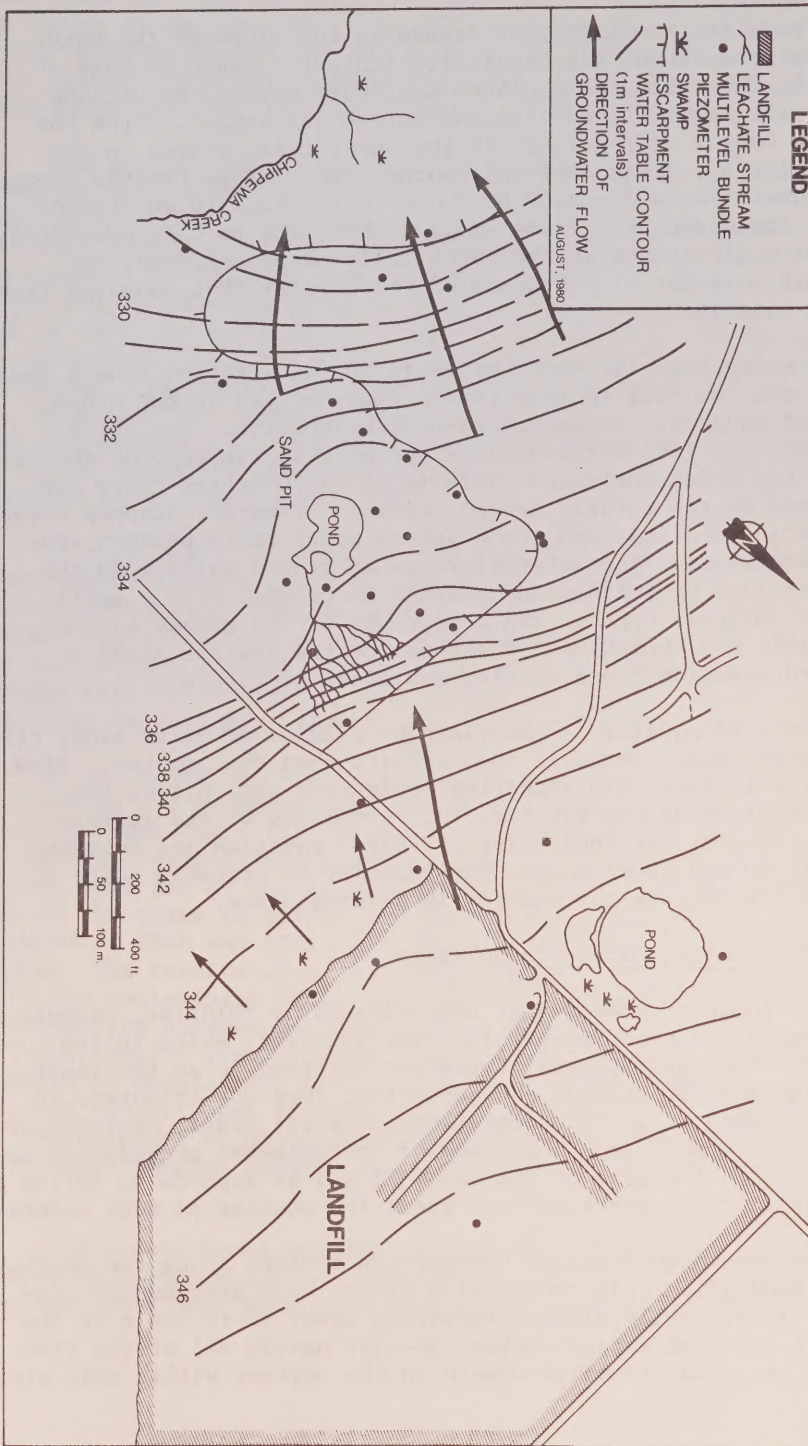


Figure 6. Hydrogeological cross section along the centre of the contaminant plume at the North Bay landfill site

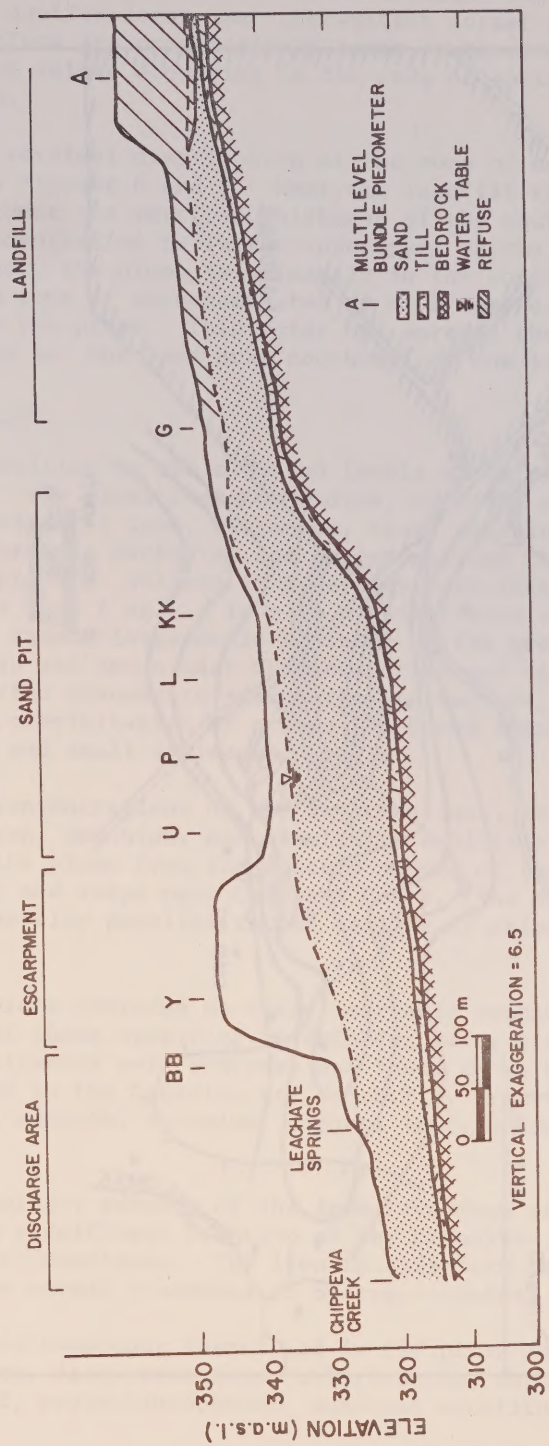
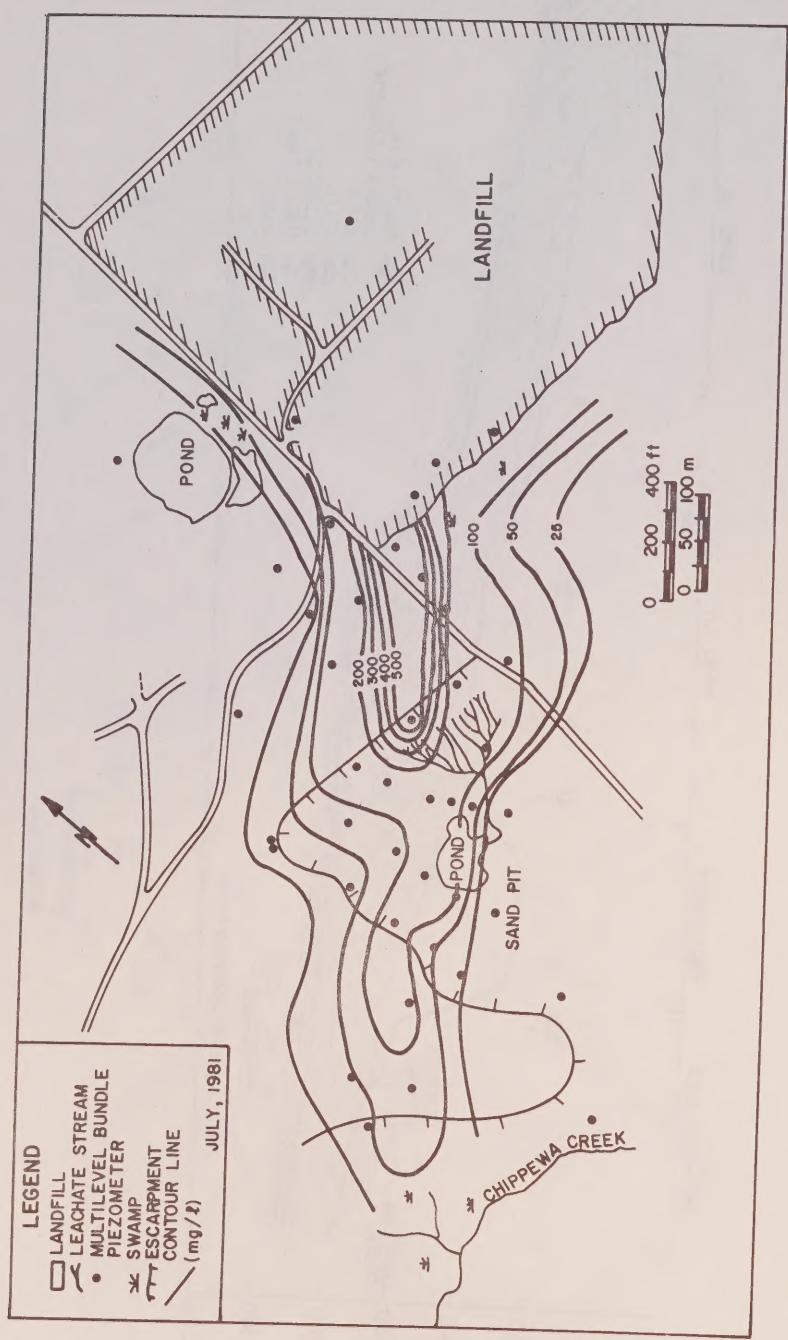


Figure 7. Distribution of the contaminant plume represented by contours of the maximum chloride concentration -- North Bay landfill



The highest concentrations of chloride and dissolved organic carbon in the aquifer occur near the western corner of the landfill. The concentrations are progressively lower southwestward in the plume with the lowest values occurring in the area of springs and seeps near Chippewa Creek.

The vertical distribution of the zone of contamination is represented in Figures 8 and 9. Near the landfill the contaminated zone extends throughout the vertical thickness of the aquifer, but the zone of highest concentration is in the upper part of the aquifer. Farther to the southwest, the plume is primarily in the bottom part of the aquifer with a zone of uncontaminated or much less contaminated water situated above the plume. This water has entered the groundwater zone as infiltration in the land area southwest of the landfill.

Plume Composition

In addition to the elevated levels of chloride and electrical conductivity the plume contains sodium, calcium, magnesium, potassium, titratable alkalinity, iron, manganese, zinc, ammonium, organic nitrogen and dissolved organic carbon at the concentrations that are much above background (Table 1). Sulfate is generally less than 20 mg/L and nitrate is less than 1 mg/L. Iron is a constituent of particular interest because it has caused large-scale staining of the groundsurface in the areas of springs and seeps near Chippewa Creek and in the sand quarry. When the iron-rich groundwater discharges to surface, the water becomes oxygenated and precipitation of orange and brown iron hydroxide occurs in the springs and small drainage channels.

The concentrations of the major cations, iron, manganese, Kjeldahl nitrogen, ammonium, and alkalinity exhibit a decline in concentration in the plume from the western corner of the landfill to the area of springs and seeps near Chippewa Creek. The trends in concentration decline are generally parallel to the decline of chloride and dissolved organic carbon.

The plume contains no toxic inorganic contaminants at levels in the excess of those specified in drinking water standards. The following constituents were analysed and found to be below the mandatory limits specified in the Canadian and U.S.E.P.A. drinking water standards: arsenic, boron, cadmium, chromium, copper, lead, selenium, silver and uranium.

Preliminary results of the investigations of metal complexing indicate that a significant fraction of the dissolved iron in the plume occurs as organic complexes. The iron in this form therefore may not take part in the normal processes of hydrogeochemical attenuation.

Organic compounds identified in the plume include: dichloroethane, chloroform, dichlorobenzenes, chlorobenzene, naphthalene, dichlorobenzoic acid, pentachlorophenol, numerous substituted benzenes and

Figure 3. Distribution of chloride along a longitudinal and a transverse cross section. See Fig. 4 for cross section locations

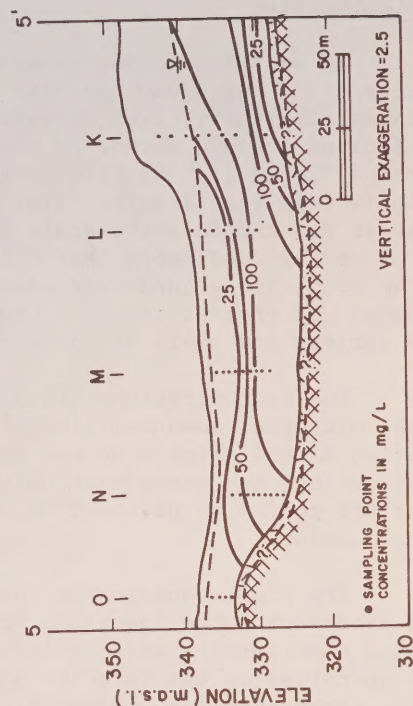
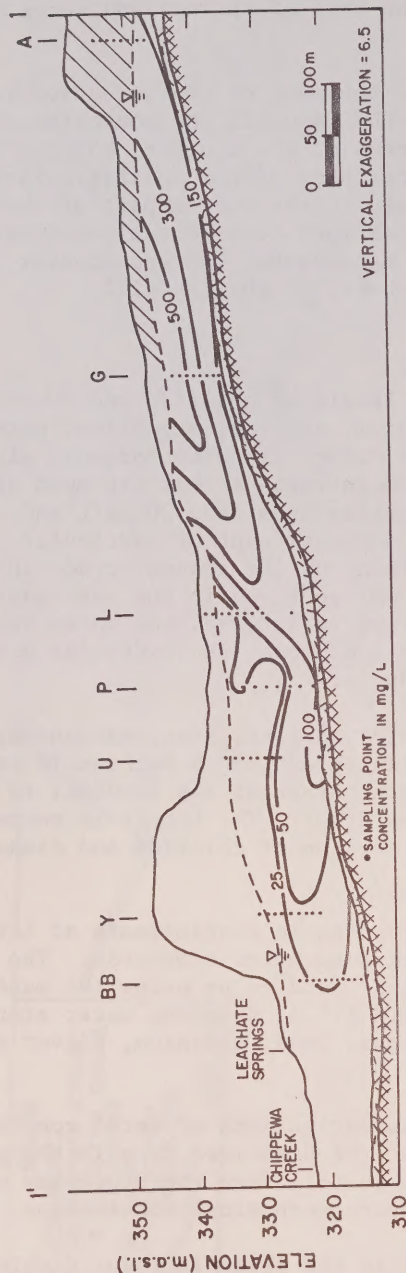
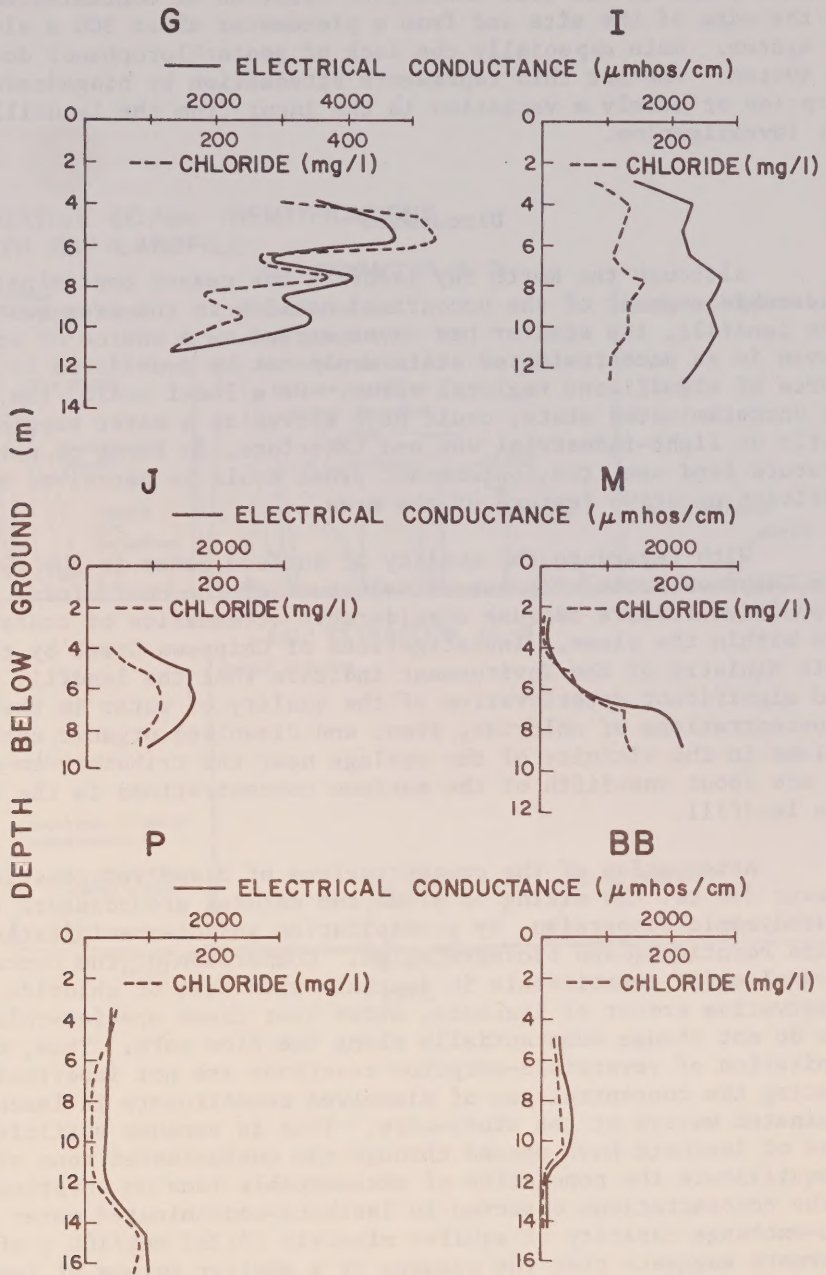


Figure 9. Vertical profiles of chloride and electrical conductance in the plume



phenols.

Figure 10 illustrates the complex spectrum of organic constituents found in the acid extraction fraction of contaminated waters from the edge of the site and from a piezometer about 300 m along the flow system. Note especially the lack of pentachlorophenol down the flow system. Whether this represents attenuation by biodegradation, adsorption or merely a variation in the input from the landfill is under investigation.

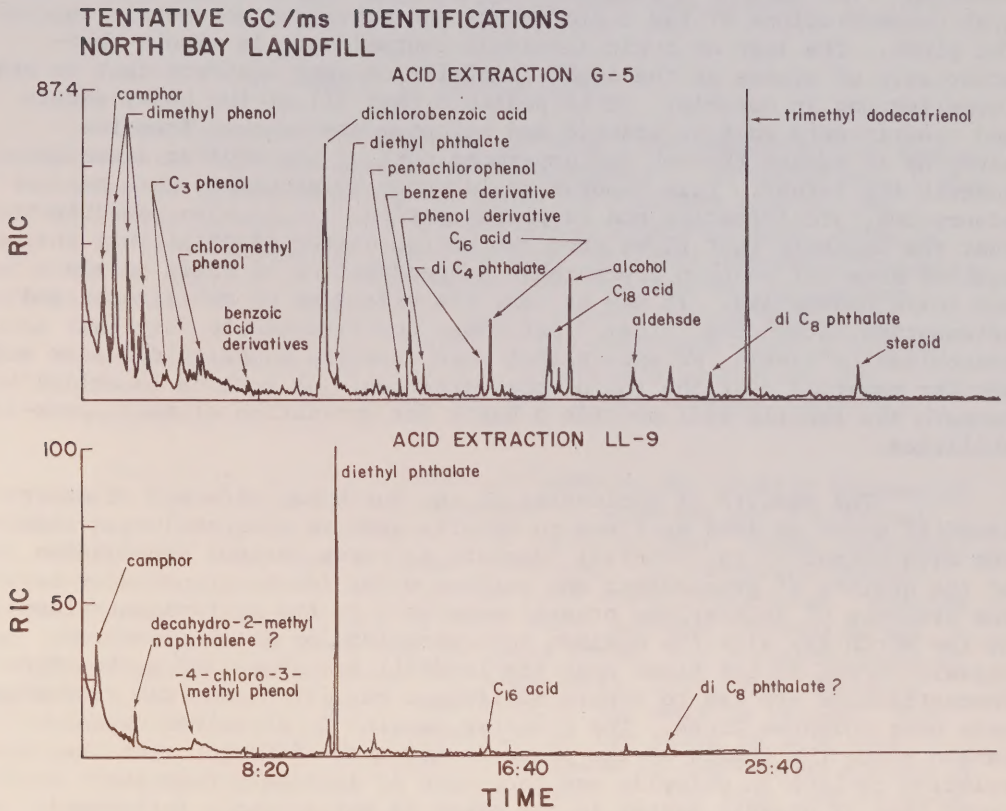
Discussion

Although the North Bay landfill has caused contamination of a considerable segment of the unconfined aquifer in the area southwest of the landfill, the aquifer has never served as a source of water supply and even in an uncontaminated state would not be considered to be a resource of significant regional value. On a local scale, the aquifer, in an uncontaminated state, could have served as a water supply for domestic or light-industrial use and therefore, in terms of potential for future land use, the contaminant plume could be perceived as a significant negative feature of the area.

With regard to the quality of surface water in the region, namely Chippewa Creek, the extensive nature of the contaminant plume is a positive feature because considerable attenuation of contaminants occurs within the plume. Investigations of Chippewa Creek by the Ontario Ministry of the Environment indicate that the landfill has not caused significant deterioration of the quality of water in the creek. The concentrations of chloride, iron, and dissolved organic carbon in the plume in the vicinity of the springs near the tributary to Chippewa Creek are about one-fifth of the maximum concentrations in the aquifer at the landfill.

Attenuation of the concentrations of dissolved constituents may occur due to: the mixing of plume and natural groundwaters induced by hydrodynamic dispersion, by precipitation and co-precipitation, sorption reactions, and biodegradation. Comparison of the concentrations of several major constituents in leachate with that of chloride ion, a conservative tracer of leachate, shows that these species-chloride ratios do not change substantially along the flow path. Thus, mineral precipitation of reversible-sorption reactions are not important in regulating the concentrations of dissolved constituents in leachate-contaminated waters at the study-site. This is because sufficient volumes of leachate have passed through the contaminated zone of aquifer to reequilibrate the population of exchangeable ions on sorption sites with the concentrations observed in leachate-contaminated water. The low cation-exchange capacity of aquifer minerals (0.265 meq/100 g of soil) furthermore suggests that the passage of a smaller volume of leachate through the flow system was required to attain the steady-state chemical evolution observed in the aquifer than if the aquifer material had a larger CEC. From the above reasoning, the attenuation of concentrations

Figure 10. Gas chromatograph/mass spectrometer traces of acid extraction fractions of heavily contaminated groundwater (G-5) and less-contaminated groundwater (LL-9). Analyses performed by the Laboratory Services Branch, Ministry of the Environment, Rexdale



of dissolved constituents in the aquifer may be attributed primarily to dispersive and biodegradation-related processes. Further monitoring during 1982 will be necessary to verify if the plume is remaining close to a steady-state condition or if the zone of high concentrations is advancing southwestward through the aquifer.

The apparent lack of significant impact of the landfill on Chippewa Creek is due to the fact that the concentrations of mobile constituents in the plume, such as chloride and iron, occur at much lower concentrations at the discharge end of the plume than near the landfill. The lack of impact can also be attributed to the absence of high concentrations of the toxic metals and inorganic non-metals in the plume. The lack of toxic inorganic contaminants is also a characteristic of plumes at the other landfills on sand aquifers that we are investigating in Ontario. It is possible that all of the heavy metals and constituents such as arsenic and selenium are removed from the water as it passes through the uppermost part of the aquifer directly beneath the refuse. This removal could occur by processes such as adsorption, precipitation and co-precipitation. It is also possible that the leachate that flows from the bottom of the landfill into the aquifer does not contain appreciable concentrations of toxic metals and toxic non-metals. It may be that the processes of mobilization and attenuation within the refuse limit these constituents to very low concentration levels. We expect that more detailed sampling of water and aquifer material near the top of the water table at various locations beneath the landfill will provide a basis for evaluation of these possibilities.

The results of monitoring at the North Bay site and at other landfill sites on sand aquifers in Ontario lead to the conclusion that the main potential for landfill leachate to cause serious degradation of the quality of groundwater and surface water fed by groundwater is the presence of deleterious organic compounds in the contaminant plumes. At the North Bay site the maximum concentrations of total dissolved organic carbon in the plume near the landfill are above 200 mg/L. The concentrations are ten to twenty milligrams per litre near the discharge area near Chippewa Creek. The relative decline in dissolved organic carbon along the length of the plume is not much different than the relative decline in chloride and therefore it is likely that the gross load of organic matter in the plume is not strongly influenced by adsorption or microbial degradation. However, specific organic compounds may be undergoing considerable attenuation along the plume.

The degree to which dissolved organic carbon causes degradation of water quality depends on the specific organic compounds that are present, the toxicity of these compounds and the extent to which the toxic compounds are attenuated in the flow system. These factors are currently being evaluated at the North Bay site as part of an interdisciplinary study of the character, subsurface mobility and toxicity of organic compounds in permeable aquifers at sanitary landfills and toxic waste disposal sites in Ontario. The organic matter is being characterized

in terms of molecular weight distributions, function groups and other properties of the higher molecular weight humic and fulvic substances. Toxic trace organics are being identified and the effects of dispersion, adsorption and biodegradation along the plumes are being evaluated. The toxicity of the contaminated groundwater is being evaluated. At North Bay, site G, L.D. 50 occurred in a mixture of 25% leachate 75% tap water. Microbial activity in the contaminated aquifer is being determined as part of the evaluation of biodegradation as an attenuation mechanism for trace organic compounds. A wide range of bacteria types have been identified in the North Bay plume. Total populations as high as 10^6 viable bacteria per gram of solids have been detected in core samples.

Summary of Conclusions

Leachate from the Woolwich and North Bay landfills has contaminated much of the local unconfined sand aquifer. At North Bay, a zone of contaminated groundwater exists along the southern edge of the landfill. This zone, which is a groundwater discharge area, extends about 50 m from the edge of the landfill. The contaminated groundwater that moves to surface in this area enters a wetland and spruce bog where it appears to be attenuated in the porous organic soil. A second zone of contaminated groundwater has developed along a 200 to 400 m wide path that extends from the southwestern corner of the landfill to an area of springs and seepage zones located about 750 m to the southwest.

This plume of contaminated groundwater was readily delineated using bundle piezometers and measurements of chloride and electrical conductance. Throughout the plume, the major cations, irons, manganese, zinc, alkalinity, ammonium, Kjeldahl nitrogen, and dissolved organic carbon occur at concentrations that are much above background. Between the southwestern corner of the landfill where maximum concentrations occur and the discharge area near Chippewa Creek, the concentrations of major constituents such as chloride, alkalinity, iron, and dissolved organic carbon decline to about one-fifth of the maximum values. This decline could be attributed to dispersion if the plume is at a near steady-state condition or to a gradual increase in the concentrations of leachate entering the aquifer at the landfill, if the high concentration zone is advancing along the plume. These possibilities will be evaluated as the results of monitoring in 1981 and 1982 are obtained.

The plume contains no significant concentrations of toxic inorganic elements. At present there are two plausible explanations: the toxic metals and non-metals such as arsenic may be removed from the leachate as it passes through the first few metres of the aquifer beneath the landfill or these constituents may not be present in the leachate as it passes below the bottom of the landfill.

A number of toxic specific organic compounds have been identified in the groundwater in the plume. Much of the emphasis in

the investigation is now being directed towards determination of the effects of adsorption and biodegradation on selected organic compounds. Carbon isotopes are being used as an aid in the identification of trends in carbon transformation from organic to inorganic states.

Acknowledgements

We extend our thanks to Paul Johnson for technical assistance in the field during all phases of the program of drilling and installation of piezometers. Assistance with water sampling and field geochemical measurements was provided by K. Morin, T. Cosgrove, S. King and A. Abdul. Funds for the hydrogeological and inorganic geochemical parts of the investigation were provided by the Lottery Trust Fund of the Ontario Ministry of Environment and by the Regional Municipality of Waterloo. A strategic Grant from the National Science and Engineering Research is making possible studies of the occurrence and transformations of organic compounds in the contaminant plume.

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THE KENNEDY-BURNETT STORMWATER TREATMENT POND STUDY
SOME PRELIMINARY RESULTS

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The first two years of the three year study are reported. The study objectives are to evaluate stormwater runoff impoundment under continuous flow and batch operation with and without chemical flocculation as a means of water quality improvement, using field sampling and computer model simulation. Parameters of interest include BOD, total phosphorus, suspended solids, and fecal coliform bacteria.

The 61 hectare study site is located about 8km south of Ottawa. Stormwater runoff was detained in a 25,000 m³ treatment pond for times up to eleven days giving varying degrees of treatment in batch operation. Suspended solids and volatile suspended solids removals usually exceeded 90%, BOD removals ranged from 20% to 70%, nitrogen species from 20% to 60% and total phosphorus was reduced by 60% to 90%, not considering seasonal variations. Fecal coliform and fecal streptococcus reductions for most events were in the 90% range. Further analysis of data obtained in 1981 will be used to confirm bacteriological die off rates. The mechanism by which bacteria are reduced is thought to be a combination of die-off, dilution and sedimentation.

Treatability of runoff indicated that with 4mg/L Fe⁺⁺⁺, it was possible to remove 80% to 90% of suspended solids and total phosphorus in ten hours of settling, whereas without flocculants, the removal was only 55% suspended solids and 35% of total phosphorus.

Further analysis of the data will be reported at the completion of the study.

THE KENNEDY-BURNETT STORMWATER TREATMENT POND STUDY
SOME PRELIMINARY RESULTS

Prepared for the Ontario Ministry of the Environment
 Technology Transfer Conference No. 2
 November 24, 1981

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The Kennedy-Burnett Stormwater Treatment Pond Study

Some Preliminary Results

A study of stormwater management within the Regional Municipality of Ottawa-Carleton was initiated in June 1979, with the funding of the Provincial Lottery Trust Fund, to study water quality problems in the Rideau River and suggest means to eliminate them. The Kennedy-Burnett Stormwater Treatment Pond Study, which was at that time being prepared by the Regional government, became a major component of the Rideau River Stormwater Management Study (RRSMS). Funding for the treatment pond study instrumentation and monitoring equipment was provided through the RRSMS, with the Regional Municipality of Ottawa-Carleton supplying the management, experienced field personnel and laboratory facilities to carry out the sampling program and chemical analysis. The Ontario Region laboratories of the federal Environmental Protection Agency performed all the microbiological and trace metal analysis. Use of the study facility and pond maintenance was through the kind cooperation of the City of Nepean.

The treatment pond study has the following objectives:

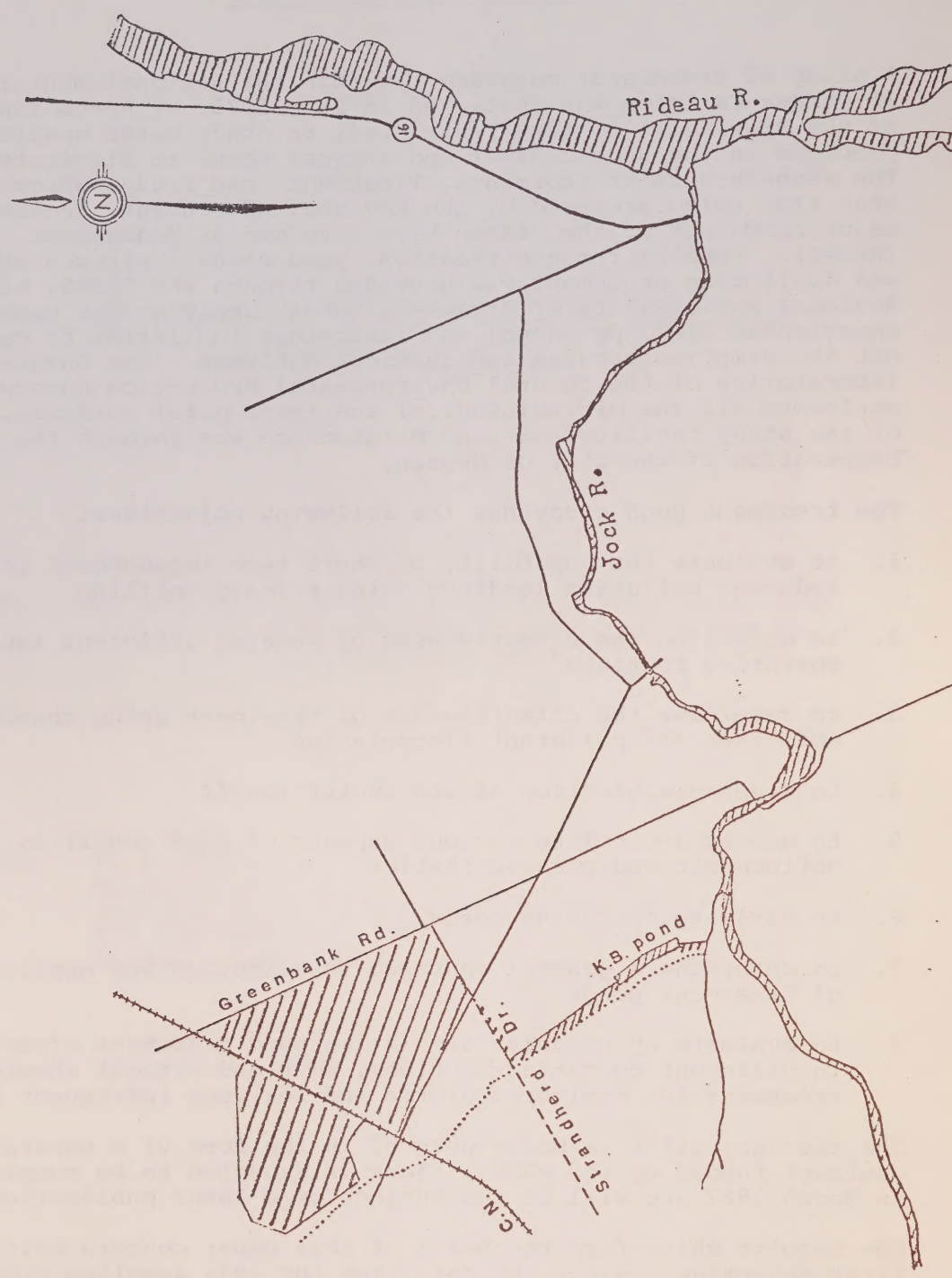
1. to evaluate the capability of short term impoundment in reducing pollutant loadings using primary settling
2. to determine the effectiveness of several different impoundment operating routines
3. to determine the effectiveness of treatment using chemical additives for pollutant flocculation
4. to study disinfection of stormwater runoff
5. to assess and relate various aspects of pond condition to performance and pond aesthetics
6. to estimate operating costs
7. to determine a general approach to selection and application of treatment ponds
8. to evaluate by computer simulation pond treatment effectiveness in different operating routines, with and without chemical treatment for monitored storms and for very infrequent storms.

The last objective is being pursued in the form of a separate contract funded by the RRSMS. Work is expected to be completed in March 1982 and will be the subject of a later publication.

The results which form the basis of this paper concern mainly the first objective. Since the data from the 1981 sampling program are still being evaluated, only a few comments will be possible on the second and third objectives.

FIG. 1

KENNEDY - BURNETT STORMWATER RUNOFF TREATMENT STUDY SITE.



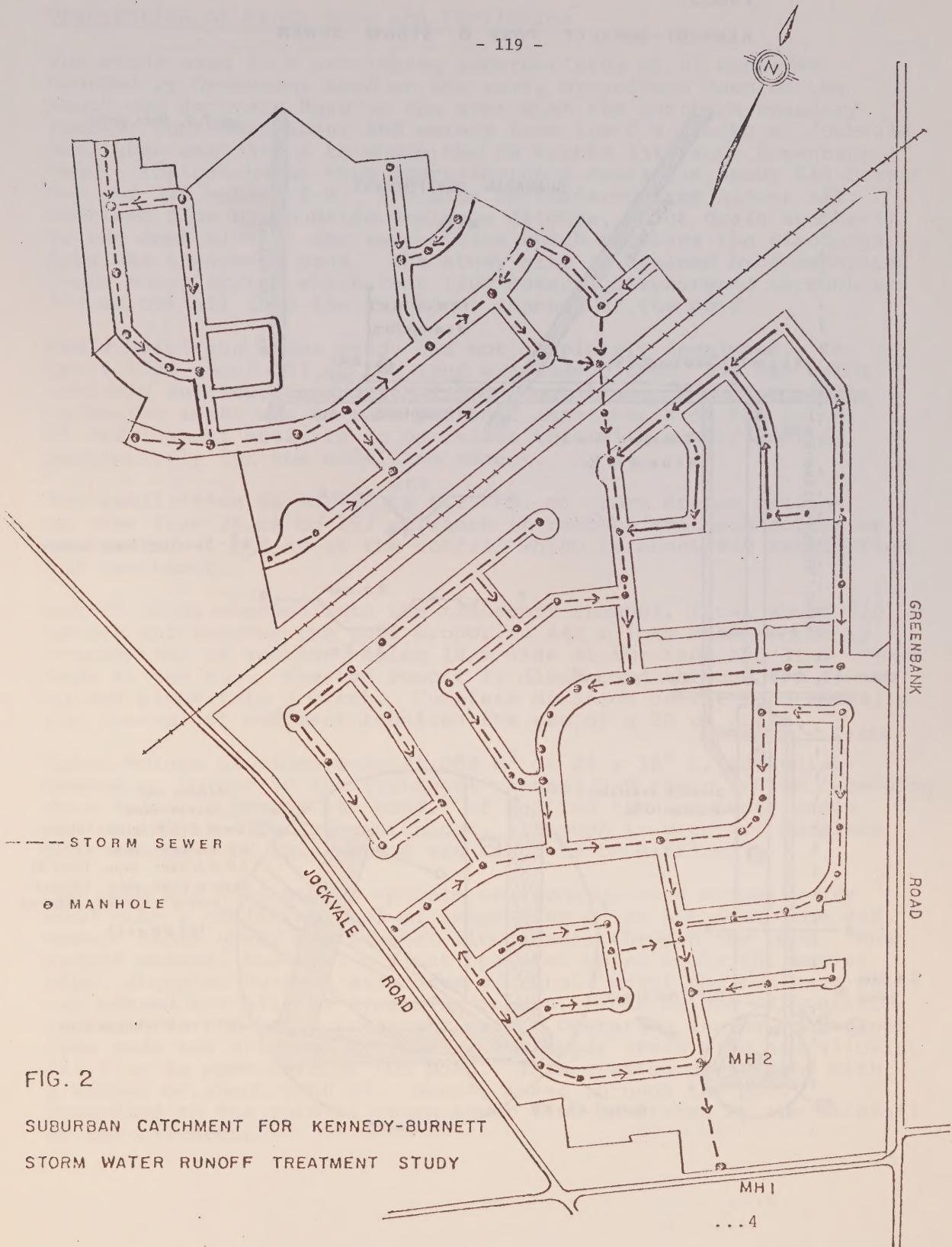
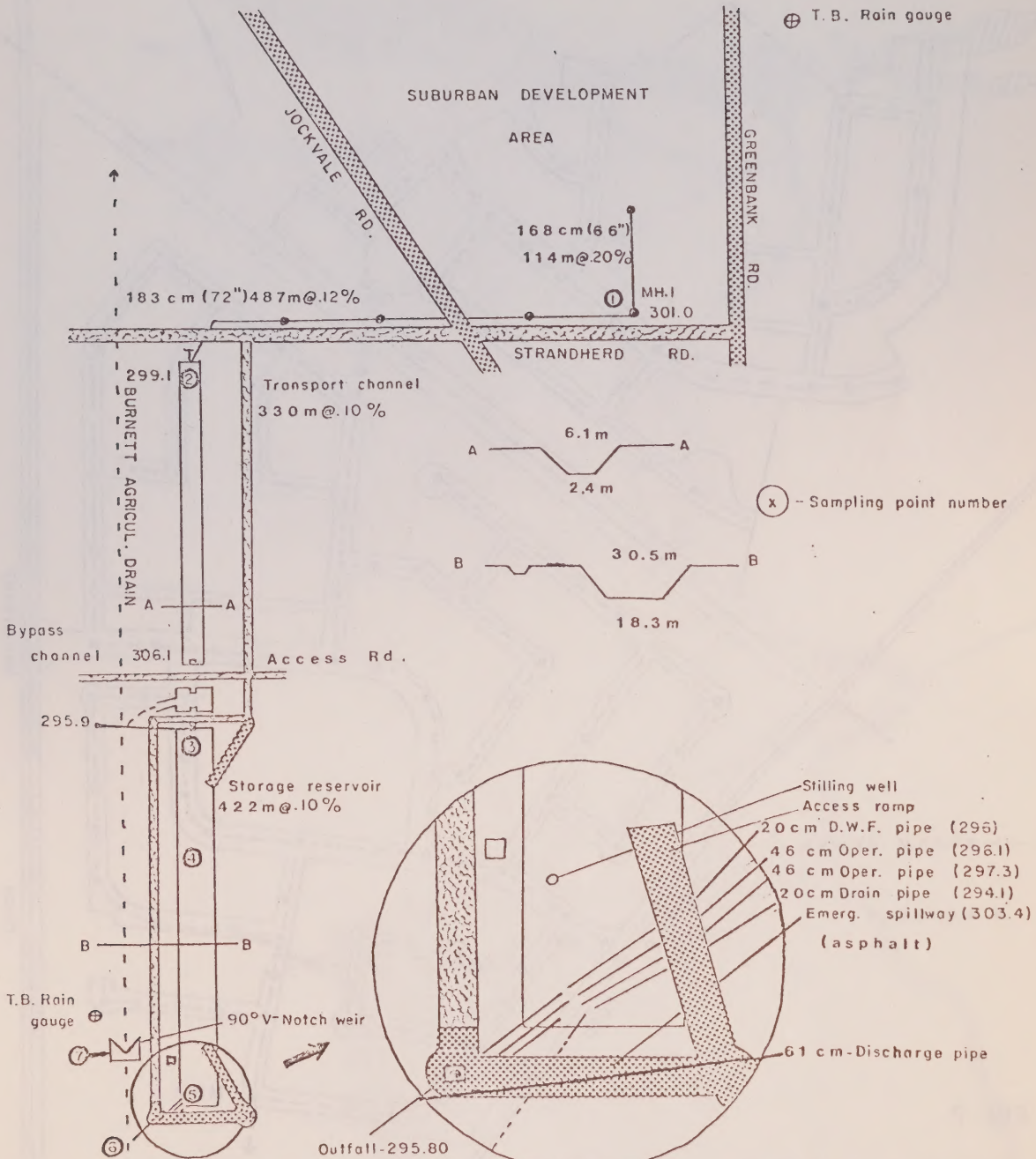


FIG. 2

SUBURBAN CATCHMENT FOR KENNEDY-BURNETT
STORM WATER RUNOFF TREATMENT STUDY

FIG. 3

KENNEDY-BURNETT POND & STORM SEWER



Description of Study Site and Facilities

The study area is a developing suburban area of 61 hectares bounded by Greenbank Road on the east, Strandherd Road on the south and Jockvale Road on the west with the northern boundary running northwest about 500 meters from the C.N tracks at Jockvale Road then east 500 m to where the CN tracks intersect Greenbank Road. The catchment thus approximates a rectangle about 610 meters N-S and 370 meters E-W. The site is isolated from almost all overland flow by roadside drainage ditches, which drain southerly to the Jock River, the same stream which receives the discharge from the treatment pond. The study site is drained by a separate storm sewer system which runs 1200 meters, discharging through a 183 cm outfall into the transport channel of the pond.

The subdivision under study was not completely developed. In April 1980 about 25% of the land was undeveloped, 23% was being actively developed and 52% had been completed. One of our data gathering tasks was to make periodic assessments of the extent of development activity to correlate this with runoff quality, particularly for the modelling aspect.

The subdivision is served by 6.25 km. of storm drains ranging in size from 26 cm to 152 cm where it reaches the main collector, increasing to 183 cm at the outfall which is about 650 meters from the catchment.

Runoff is discharged into the transport channel, flows about 330 meters and reaches the pond proper, a 442 m long basin which is trapezoidal in section, being 18 m wide at the base and 31 m wide at the top. Treated runoff is discharged through two 46 cm valved pipes into a ditch. Complete drainage of the pond normally for removal of sediment requires the use of a 20 cm drain.

Total volume of storage is $25,000 \text{ m}^3$ or $25 \times 10^6 \text{ L}$, including backed up volume in the transport channel and sewer. Flow exceeding this volume bypasses the pond. If desired the treatment basin can be isolated by using stoplogs, although in practice complete flow stoppage by this method was found to be difficult.

The pond was designed to operate unattended, as a normally dry pond with a polishing pool of about 2000 m^3 at the discharge end. Normal storm sewer dry weather flow passes through the pond. When runoff enters, however, a float operated valve seals the outlet pipe, stopping further discharge of runoff until the drainage pipes are opened manually or bypassing occurs. This method of operation is known as the batch treatment mode. Operation in the continuous flow mode was effected by opening the upper drain pipe and allowing all flow to pass through the pond. This created a wet pond with a volume of about 6000 m^3 . Runoff moved through the pond depending on the rate of storm sewer flow generated by the rainfall on the catchment.

VOLUME STORED IN POND $\times 10^6$ I.G.

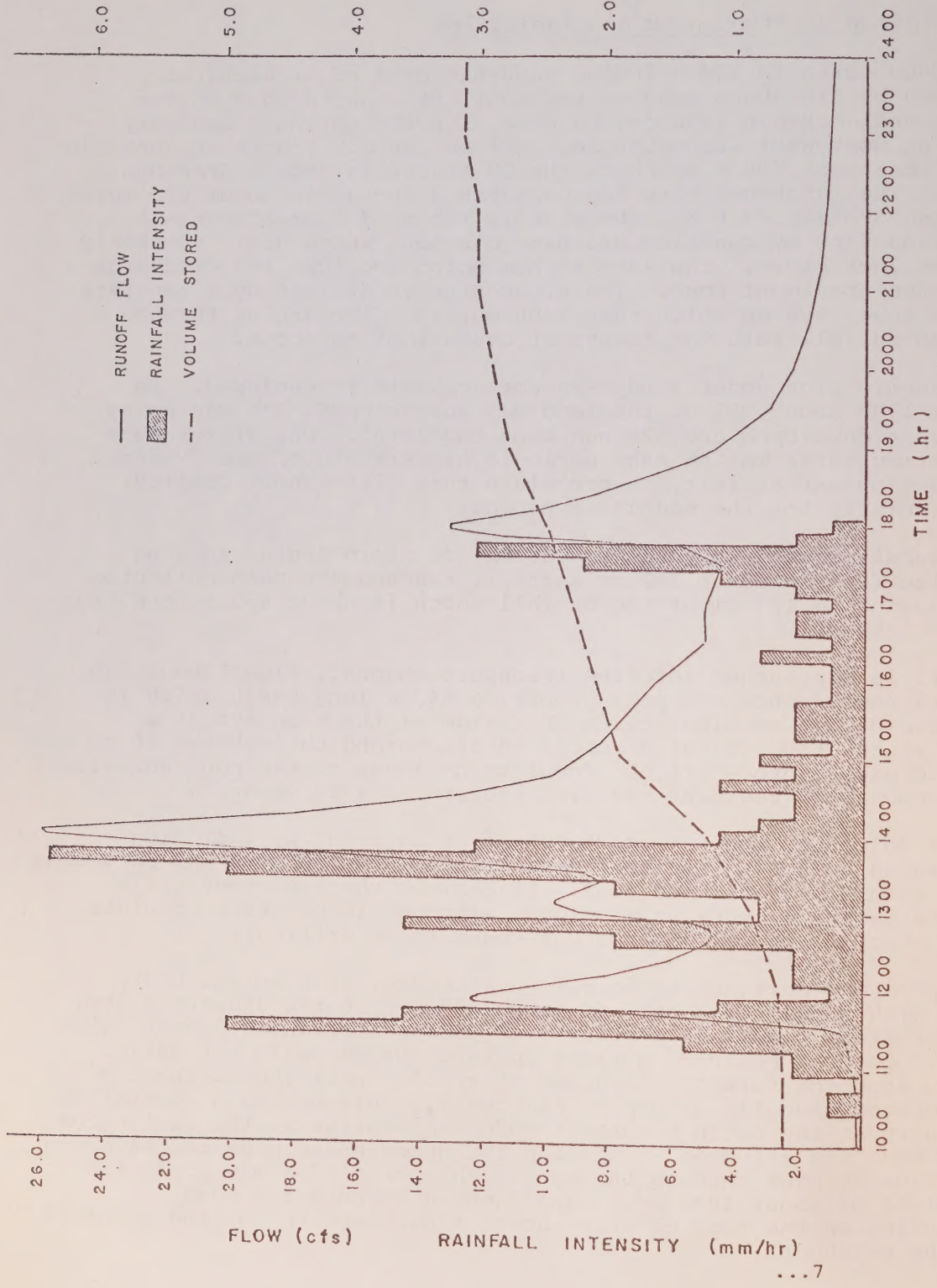
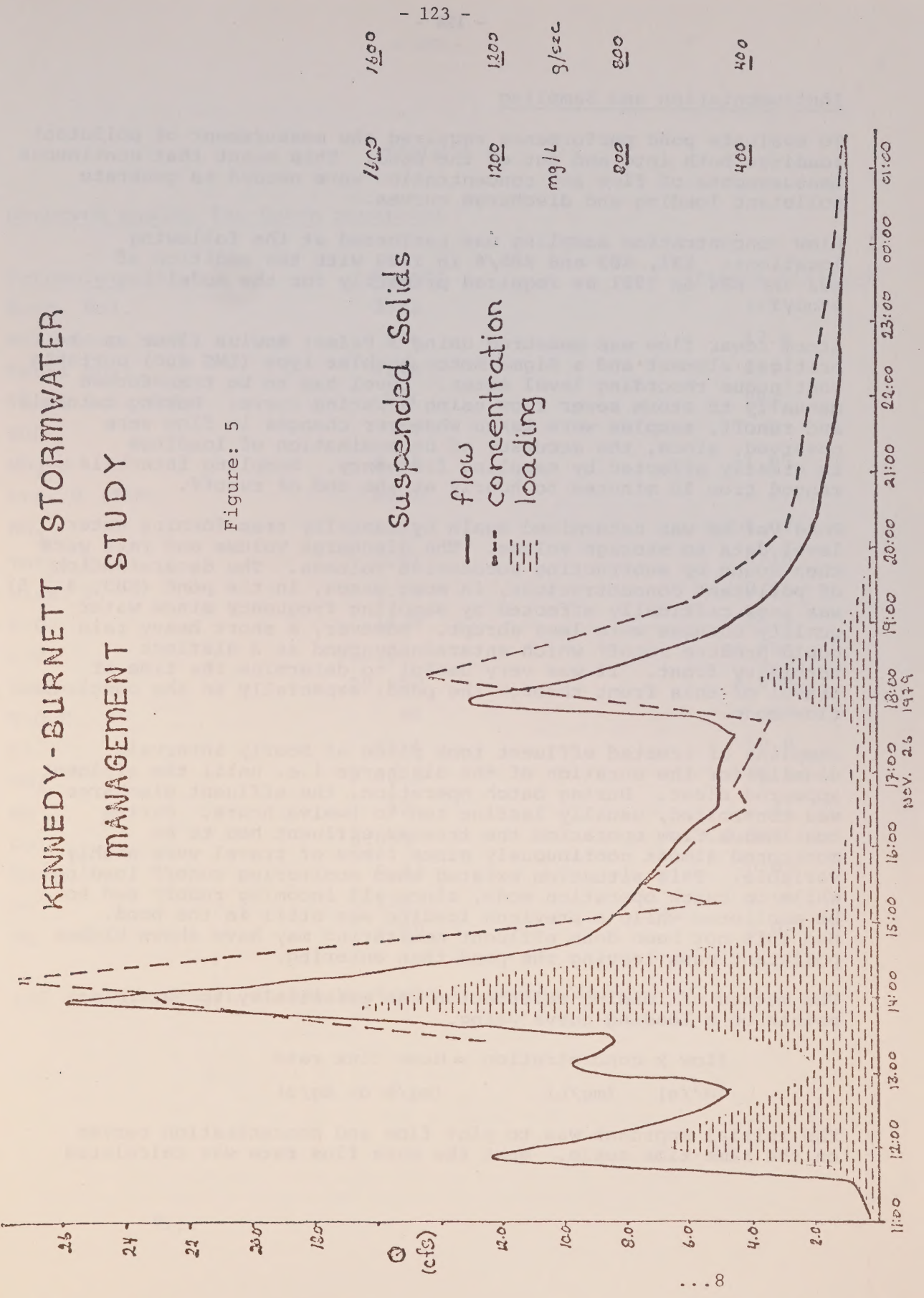


FIGURE 4: RAINFALL EVENT - NOVEMBER 26, 1979.

KENNEDY-BURNETT STORMWATER MANAGEMENT STUDY

Figure: 5



Instrumentation and Sampling

To evaluate pond performance required the measurement of pollutant loadings both into and out of the pond. This meant that continuous measurements of flow and concentration were needed to generate pollutant loading and discharge curves.

Flow concentration sampling was performed at the following locations: KB1, KB3 and KB5/6 in 1980 with the addition of KB2 and KB4 in 1981 as required primarily for the modelling study.

Storm sewer flow was measured using a Palmer Bowlus flume as the critical element and a Sigma motor bubbler type (LMS 400) portable continuous recording level meter. Level had to be transformed manually to storm sewer flow using a rating curve. During rainfall and runoff, samples were taken whenever changes in flow were observed, since, the accuracy of determination of loadings is greatly affected by sampling frequency. Sampling intervals ranged from 10 minutes to hourly at the end of runoff.

Pond volume was determined again by manually transforming water level data to storage volume. The discharge volume and rate were then found by subtracting successive volumes. The determination of pollutant concentrations, in most cases, in the pond (KB3, 4, 5) was less critically affected by sampling frequency since water quality changes were less abrupt. However, a short heavy rain could produce runoff which entered the pond as a distinct turbidity front. It was very useful to determine the time of travel of this front through the pond, especially in the continuous flow mode.

Sampling of treated effluent took place at hourly intervals usually for the duration of the discharge i.e. until the effluent appeared clear. During batch operation, the effluent discharge was controlled, usually lasting ten to twelve hours. During continuous flow operation the treated effluent had to be monitored almost continuously since times of travel were highly variable. This situation existed when monitoring runoff loadings while in batch operation mode, since all incoming runoff had to be monitored while a previous loading was still in the pond. Had this not been done effluent monitoring may have shown higher pollutant mass leaving the pond than entering.

The method of loading calculation was essentially to determine points on a loading curve using.

flow x concentration = Mass flux rate

(m³/s) (mg/L) (mg/s or kg/s)

The initial approach was to plot flow and concentration curves on the same time scale. Next the mass flux rate was calculated

TABLE I

Observed Maxima for Batch Treatment

<u>Parameter</u>	<u>Runoff</u>	<u>Treated Effluent</u>
Susp. Sol.	3548	377
Vol. Susp. Sol.	546	12.6
Total Sol.	4148	564
Total Vol. Sol.	576	287
BOD	37	8
NO ₃ -N	3.98	1.65
Org. N (TKN)	10.1	2.2
NH ₃	1.21	< 0.02
Total P.	5.61	0.16
Diss. P.	0.58	0.06
D.O.	14.8	14.5
T.C.	320,000	24,000
F.C.	79,000	3,000
T.O.C.	96	18
Cl ⁻	65.6	50.0
SO ₄	90.0	65.5
Mg	52	21
Cu	0.055	< 0.005
Pb	0.21	0.05
Fe	120	2.50
Hg	0.22	0.05

All values in mg/L except bacteria in counts/dL.

by taking the product of flow and concentration, resulting in a curve of loading rate variation with time. This curve was integrated to produce the total mass flux over the time of the event. Doing this work manually became very tedious because of the large number of parameters and data points, so a programmable calculator was used, eliminating the graphing and integrating steps. The same approach was used in calculating treated effluent loadings, although in this case it was often possible to use the average concentration over a long time interval (3 hours or more) because quality and flow variations were small.

The data obtained in 1980, reflect pond operation in the batch mode. Results obtained in 1981, which are not yet available for discussion here, will show the effectiveness of continuous flow pond operation.

Study Results

An overview of treatment effectiveness can be obtained by looking at the difference between polluted runoff and treated effluent quality. Because retention times vary, the comparison can be made across all the events observed, and is shown in Table I. For every parameter, the treatment pond effluent was of significantly higher quality than the stormwater runoff, indicating that the batch treatment mode was effective overall.

The most useful indicator of treatment effectiveness, however, is pollutant loading reduction to the receiving water, or loading removal from runoff. Table II compares loading data from various storms monitored in the batch mode. Also indicated are characteristics of the various runoff events which are significant factors in evaluating pond performance.

The storms represent a wide range of total precipitation and intensities. The total volume of runoff is the measured storm sewer flow which includes a baseline volume of storm sewer flow. The total volume treated is the total of runoff plus baseline flow which entered the pond over the time from the start of runoff flow until beginning of discharge of treated effluent. The events beginning June 20, 1980 and July 15, 1980 consisted of contributions from four and three events respectively.

In these cases treated runoff could not be discharged before other rain occurred, and so all input loadings were monitored. Separation of the events within the pond was not possible because of mixing. As a result one treated effluent discharge took place for each event. The total loading for June 20 to 27 was 2460 kg of suspended solids while discharge was 17 kg. For the July 15 to 17 events the total suspended solids loading was 79 kg with 11 kg discharged.

The percent removal of various parameters makes up the body of the table. Very good removal of suspended and volatile suspended

TABLE II
 RUNOFF EVENT AND POLLUTANT REDUCTION
 Batch Operation Mode

Event Characterization	1979		1980						1981		
	Sept. 14	Nov. 26	20	June 23	June 26	27	15	July 17	Aug. 27	Sept. 2	Aug. 5
Total Percip (mm)	57	38	3	8	3	11	6	3	20	17	80
Max. Inten. (mm/hr.)	13	26	6	26	5	31	14	5	45	65	65
Tot. Q L x 10 ³	7226	9030	290	638	180	596	175	244	910	1300	14,545
Retention (days)	4.5	11	7	3.5	1.2	0.7	2.2	0.2	2.5	3.3	4
Parameter	% Removal										
S.S.	89	98		99				86	98	94	96
V.S.S.	83	95		99				66	96	--	--
B.O.D.	34	18		56				20	73	-24	38
NO3	51	-11		78				63	93	51	54
T.K.N.	58	67		60				--	74	13	33
T.P.	59	74		94				25	94	82	77
F.C.	--	--		89				--	99	96	100.
F.S..	--	--		97				93	99	99	100.
Zn	--	--		77				--	55	24	--
Pb	--	--		80				--	73	84	--

SETTLEABILITY

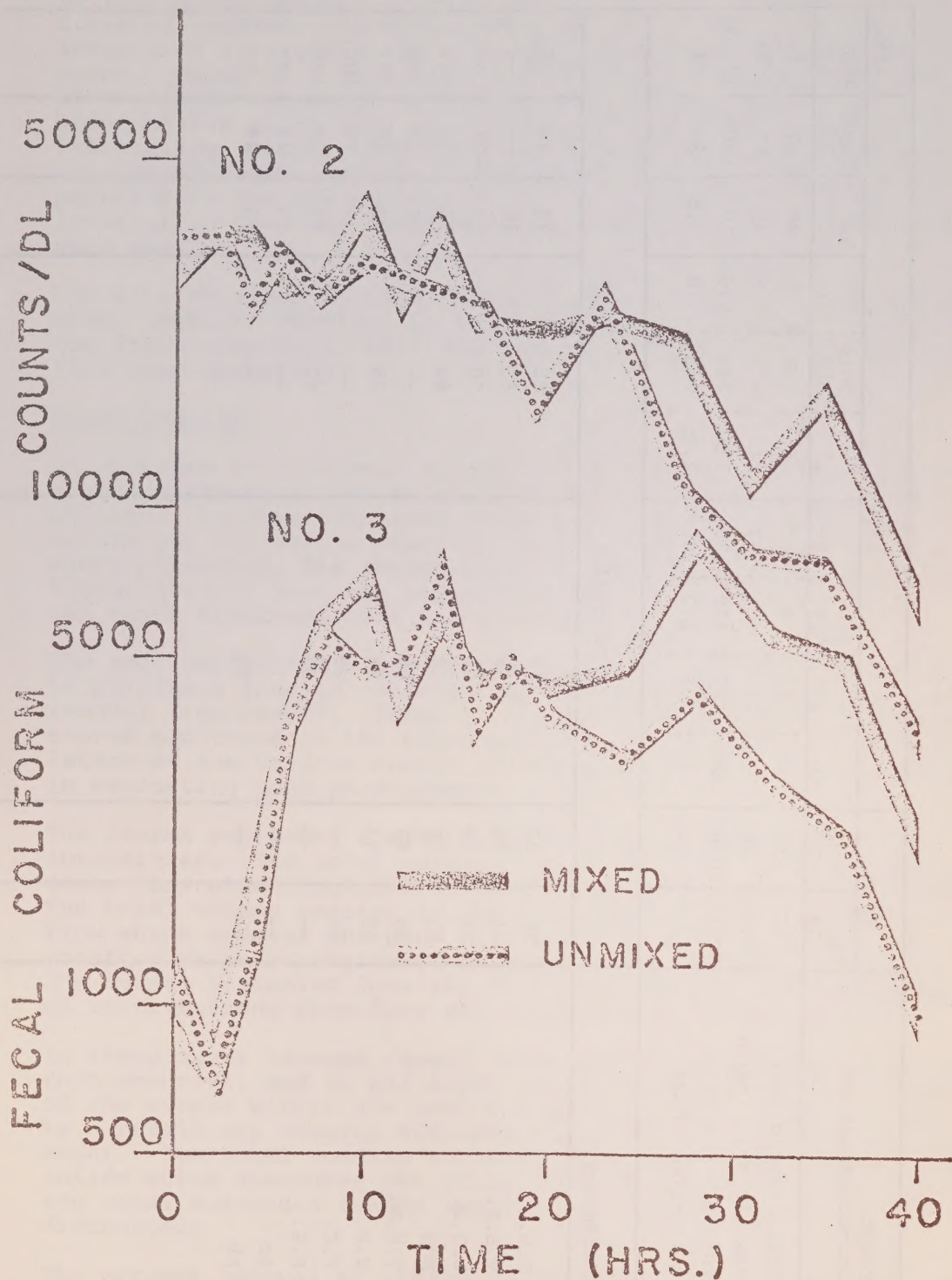


FIGURE 6

RUNOFF TREATABILITY

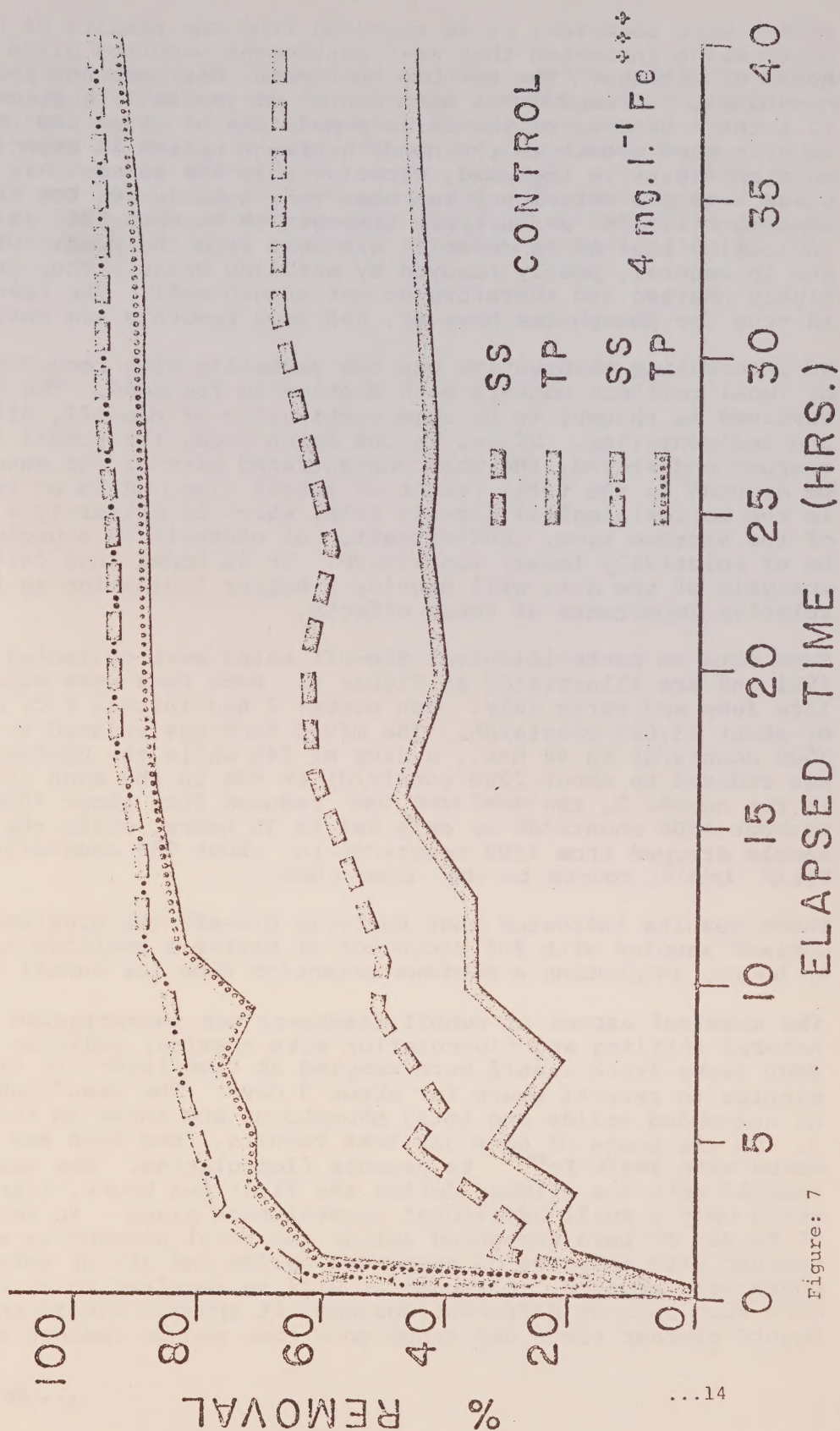


Figure: 7

solids were observed, as we expected from the results of treatability tests which indicated that most settlement occurred given 12 to 15 hours of storage. The soluble nutrients, nitrogen and phosphorous compounds, both exhibited a high degree of variability from event to event. Because of the large population of algae and rooted aquatic weed growth in the pond, nutrient uptake is expected to be significant in the pond, especially in the summer. In some cases negative efficiency was observed, notably for BOD on September 2, 1980 and nitrate nitrogen on November 26, 1979, indicating that extra material was lost from the pond. Nitrates are in general, poorly removed by settling because they are not highly charged and therefore do not adsorb well. The reverse is true for phosphates however, and good removals are observed.

An interesting observation was the generally high reduction of fecal coliform numbers with storage in the pond. The mechanism involved is thought to be some combination of die-off, dilution and sedimentation. Since, in the batch mode, the runoff is all trapped and stored, the most concentrated part of the runoff will be diluted in the total volume of runoff flow. Also of importance is the bacteriological die-off rate, which is primarily a function of the storage time. Sedimentation of bacteria is expected to be of relatively lesser importance. It is hoped that further analysis of the data will provide a better indication as to the relative importance of these effects.

Some data on bacteriological die-off rates were collected in 1981 and are illustrated in Figure 6. Both runs were made in late June and early July. Run number 2 had initial F.C. counts of about 33,000 counts/dL. The mixed tank was reduced to about 8500 counts/dL in 48 hrs., a drop of 74% while the unmixed tank was reduced to about 2200 counts/dL or 93% in the same time. In run number 3, the mixed tank was reduced from about 7000 counts/dL to about 4500 counts/dL or only 36% in 35 hours, while the unmixed sample dropped from 5200 counts/dL to about 950 counts/dL or 81% of initial counts in the same time.

These results indicated that bacteria die-off was greatest in the unmixed samples with 90% reduction of bacteria possible in roughly 48 hours, suggesting a minimum retention time for runoff storage.

The chemical aspect of runoff treatment was investigated for both natural settling and flocculation with chemical addition. Two 200L tanks fresh runoff were sampled at time intervals from 15 minutes to several hours for about 3 days. The resulting removal of suspended solids and total phosphorus are shown in Figure 7. On the basis of some jar test results, one tank was dosed with 4mg/L Fe^{+++} to promote flocculation. The maximum removal rate was evident during the first ten hours, after which only a small additional removal took place. In ten hours 80 to 90% of both suspended solids and total phosphorus were removed with only 55% of suspended solids and 35% of total phosphorus removed. Although it will be required to carry out more such runs at different dosages, it appears likely that runoff storage times and hence pond size can be reduced by using

chemically augmented flocculation. Before the initial estimate of two days' storage can be reduced, however, several other questions remain to be answered. The change in bacterial concentration with the application of coagulants in the pond needs to be determined. Also, the full scale dosing of runoff may result in different removal efficiencies than our tank studies have shown, because the pond operation is dynamic. These areas have to be explored through the field trials.

SEWAGE EFFLUENT TREATMENT

IN AN

ARTIFICIAL MARSHLAND

BY:

S. A. BLACK, I. WILE, G. MILLER

ONTARIO MINISTRY OF THE ENVIRONMENT

FORMERLY PRESENTED AT THE

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Sewage Effluent Treatment in an Artificial Marshland

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ABSTRACT

Sewage lagoons are a common means of wastewater treatment for smaller Ontario communities. Frequently, the capacity of receiving waters to accept effluent from such facilities is limited by inadequate dilution during summer low flow periods leading to nuisance proliferation of plants and algae, with attendant widely fluctuating oxygen levels. Storage of effluent during periods of low flow requires large areas of land, and replacement of lagoons with mechanical treatment systems is very costly for small municipalities. Natural or artificial marshlands may provide a viable treatment alternative.

To determine the potential of wetlands for year-round sewage treatment in Ontario, an experimental study using an artificial marsh was established in 1979. The study is designed to define the degree of pretreatment required prior to waste discharge to wetlands, maximum loading rates, required retention periods and depths of liquid to establish optimal operational limits for these types of systems.

The artificial marsh has been constructed at the site of the Listowel sewage lagoon which consists of an aeration cell and two lagoons operated in series. The experimental marsh consists of five separate systems as well as a small control marsh for monitoring rates of evapotranspiration. Systems I, II and III receive effluent from the east lagoon, the first in series, while Systems IV and V receive aeration cell effluent. System I consists of a deep pond, a shallow marsh and a channelized marsh operated in series, Systems III and V are channelized marshes, and Systems II and IV are shallow marshes. The channelized and open marshes are planted with cattails, *Typha* spp.

Each system is capable of operating at flow rates of 0.5 to 2 times average design and at various depths and retention times. Flows are controlled and measured by V-notch and rectangular weirs and water level recorders. Routine parameters (i.e. nutrients, BOD₅, etc) are monitored on a weekly basis in all influent and effluent streams.

This paper presents data on the first full year's operation of the artificial marsh, including loadings, removal efficiencies and effluent qualities of the various systems.

Preliminary data suggest that artificial marshes have the capacity to improve the quality of partially treated wastewaters; the degree of improvement being dependent upon many factors including hydraulic loading, retention time, season and system configuration.

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1.0 INTRODUCTION

Effluent requirements within the Province of Ontario are determined under the provisions of a document "Water Management, Goals, Policies, Objectives and Implementation Procedure of the Ministry of the Environment"¹. In accordance with the policies outlined in this publication, effluent requirements are established on a case-by-case basis considering the characteristics of the receiving water body, as well as Federal and Provincial effluent regulations and guidelines, if they apply.

For discharges from municipal and private sewage treatment works, Provincial jurisdiction applies, except for Federal facilities. Normally, however, the Federal government consults with the Province to ensure that the effluent from Federal plants will be consistent with Provincial policies. Secondary treatment is considered as the normal level of sewage treatment required in the absence of detailed receiving water assessments.

Sewage lagoons are a common means of secondary sewage treatment for the smaller communities of Ontario. Lagoons are popular in such situations because of their low capital and operating costs, simplicity of process and minimal maintenance requirements.

Frequently, however, such small communities are situated on small streams or rivers. The capacity of such receiving waters to accept sewage effluent is often limited by inadequate dilution during summer low flow periods. Such conditions can lead to excessive fertilization leading to nuisance proliferation of plants and algae, with attendant widely fluctuating oxygen levels. In addition, elevated ammonia and hydrogen sulphide concentrations in winter and early spring discharges from sewage lagoons frequently exceed levels toxic to fish.

1. Ontario Ministry of the Environment Publication, 135 St. Clair Ave. W., Toronto, Ontario M4V 1P5

To overcome this problem, many sewage lagoon systems have been converted to, or were designed as, seasonal retention lagoons. These systems provide storage of lagoon contents during the low stream flow period of the summer to overcome inadequate dilution. In some instances, seasonal retention lagoons have been provided with low level, subsurface aeration for hydrogen sulphide control during the winter and early spring periods.

Sewage lagoons may also be replaced with mechanical, tertiary sewage treatment facilities to provide a high degree of treatment, thereby permitting year-round discharge.

Conversion of continuous discharge lagoons to seasonal retention lagoons, and expansion of the same, are very land consumptive and in many areas, compete for high value agricultural lands. Replacement of lagoons by mechanical plants is costly and frequently impractical for these small communities.

In recent years, the potential of aquaculture and land application approaches to wastewater treatment have received renewed and increasing attention in North America. It has been suggested that biological treatment systems, such as marshes and wetlands, are capable of removing organic and inorganic wastewater constituents, degrading toxic compounds such as phenols, and attenuating pathogenic organisms. To date, however, attention has largely focused on the use of natural wetlands for tertiary treatment purposes, while the development of artificial marshland treatment systems has received little attention to date. Artificial marshes, however, may be a viable solution for small communities where existing sewage lagoons could in part be converted to marsh treatment systems.

To assess the potential of artificial marshlands for upgrading sewage effluent to permit year-round discharge in Ontario, an experimental marshland facility was constructed in 1979 adjacent to the existing sewage works for the Town of Listowel. Detailed studies are being conducted to attempt to define both the effectiveness of, and optimum design and operational criteria for artificial marsh treatment systems.

This paper is not a literature review of works published to date, but is rather a description of the first full year's operation of the Listowel artificial marshland facility. The paper presents data, including loadings, effluent qualities and removal efficiencies of various parameters, and relates these to the various operational modes encountered. Preliminary conclusions relating to the potential of artificial marshlands for the further treatment of sewage effluents are made.

2.0 DESCRIPTION OF STUDY FACILITY

The sewage treatment works for the Town of Listowel is a sewage lagoon system consisting of an aeration cell of 3.5 days detention followed by two facultative lagoons, each with a detention time of 35 days at the present flow rate of some $5,448 \text{ m}^3/\text{day}$. The two lagoons can be operated either in series or in parallel and are currently operating in series. The influent wastewater consists of that from the light industrial Town of Listowel and that from a canning industry, with the canning industry producing about 58% of the flow and 78% of the BOD load.

Effluent discharge is continuous in the winter but because of restrictive receiving water conditions, no discharge is permitted during the period May through August. Consequently, the lagoons are drawn down in the early spring and once filled, the contents are spray irrigated on adjacent land. Aluminum sulphate is added at a concentration of about 60 mg/l to the raw sewage from September to May to provide phosphorus removal to an effluent value of <1 mg/l during the period of continuous discharge.

The existing facility is becoming hydraulically overloaded and projected population growth dictates facility expansion. Plans for expansion have attracted special attention since established methods of sewage treatment are unlikely to resolve all of the evident water quality problems in the receiving watercourse at a reasonable cost. This made Listowel a receptive candidate for the artificial marshland study.

Construction of the artificial marsh system commenced in the fall of 1979 and was completed in July of 1980. The facility, located adjacent to the existing lagoons, consists of five separate treatment systems and a small control marsh for monitoring rates of evapotranspiration (Figure 1). System I consists of a $2,120 \text{ m}^2$ open marsh, a 728 m^2 pond and a $1,000 \text{ m}^2$ channelled marsh totalling 334 m in length, all connected in series. The berms of the channelled marsh have been designed to accommodate a tractor with a cutting bar for purposes of harvesting the marsh vegetation, with the inside width of the channels being about 3 m. System II consists of a $1,000 \text{ m}^2$ open marsh and System III of 334 m of channels. Systems I, II and III receive wastewater from the east lagoon, the first of the two in series.

Systems IV and V are duplicates of Systems III and II but receive wastewater from the aeration cell outfall.

The 28 m² control marsh is lined with plastic to prevent exfiltration (or infiltration) and receives lagoon effluent. All the other cells, except the pond, were compacted, backfilled with a mixture of subsoil, topsoil and 10% peat by volume and planted with cattails, Typha spp. The pond was compacted and seeded with pondweeds, Potamogeton spp. and Elodea canadensis.

Wastewater from the east lagoon and aeration cell are pumped to separate flow-splitting chambers and fed by gravity to the various experimental cells. Flows are controlled by V-notch and rectangular weirs. All systems are extremely flexible being capable to operating at variable hydraulic loads, retention times and depths.

All marshes are capable of being operated at liquid depths varying from 5 to 30 cm. The pond is maintained at a liquid depth of 0.9 m.

Outflows from all experimental cells are monitored by V-notch weirs and water level recorders, whereas, the influent flows are set and maintained at constant rates. This is accomplished through the use of broad crested bypass weirs in the flow-splitting chambers. Effluents from all systems are collected in a wet well and can be discharged by gravity directly to the Chapman Drain which flows into the Middle Maitland River, however, if they are of unsuitable quality for direct discharge, they can be pumped back into the west lagoon. Combined flows from Systems I, II and III, and combined flows from Systems IV and V, can be handled separately in either of the above manners if desired.

A full instrumented weather station is equipped to monitor nutrient inputs from rain and snowfall.

To permit continuous winter operation of the systems, perforated pipes connected to an air blower were installed in the culverts connecting the channels of Systems I, III and IV. All effluent chambers were insulated and heated to prevent freezing and blockage of the outflow chambers and weirs.

3.0 SAMPLING PROCEDURES AND ANALYTICAL METHODS

Sampling stations were established at all outflow weirs and inside the flow-splitter chambers for the two influents. Routine parameters (i.e. BOD, SS, nutrients, temperature, pH, alkalinity, bacteria) are monitored weekly from April to November on grab samples and at 2 week intervals for the remainder of the year. *Salmonella* populations are assessed six times per year and *Clostridium perfringens* and *Yersinia enterocolitica* are monitored during the winter months. Heavy metals are monitored on monthly samples and PCB's and organochloride pesticides every six months. Analytical techniques used are as discussed elsewhere (Ontario Ministry of the Environment, 1981). Flow measuring and sampling locations are as identified on Figure 1.

4.0 OPERATION

Following completion of construction in July, 1980, the systems were fed their respective sewage effluents at a low rate and the marshes were planted with cattails, *Typha* spp. collected from local, natural marsh areas at approximately 1 m spacings. Within two months, the growth was dense and luxuriant, suggesting that cattails are ideally suited for this type of operation.

A liquid depth of 14 cm was selected for the initial phase of operation (August to December) in all units except the deep pond of System I. Hydraulic loadings during this period were monitored as close as possible to $90 \text{ m}^3 \text{ day}^{-1}$ for System I and $17 \text{ m}^3 \text{ day}^{-1}$ for the remaining systems. These loadings gave an 11 1/2 day retention period in System I, 7 3/4 days in Systems II and V and 8 3/4 days in Systems III and IV.

In early December, water depths in the marshes were increased to 28 cm with concurrent increases in hydraulic loadings in an attempt to prevent freezing during winter operation. These changes in operation reduced the retention time in System I to 7 1/2 days, in Systems II and V to 5 days and in Systems III and IV to 6 days.

During the latter part of December, 1980 aeration tubing was installed in the connecting culverts of the channeled marshes and heaters installed over the outflow chambers in anticipation of winter freezing problems. At this time, severe ice formation in the marshes had a drastic impact on their retention periods. By late January, 1981, retention times were reduced to less than 2-3 days in Systems II to V and to 3 1/2 days in System I.

In May of 1981, flows were readjusted to provide a nominal 7 day retention period and operating depth of 20 cm in all systems.

On July 24, 1981, the flows were once again adjusted, this time to provide the same retention times used in the fall period of 1980. Liquid depth was maintained at 20 cm. Dye tests carried out on the marsh systems in early July had determined the retention times to be considerably less than those calculated from volumes. It was then realized that the stalks of the dense cattails reduced the marsh volumes by between 1/3 and 1/2 the calculated values. Actual flow rates and calculated retention times are presented later in Section 5.0, Table 1.

As mentioned previously, the channelled marshes were designed to permit harvesting. A specially designed tractor mounted harvester, consisting of a cutting bar and conveyor, was constructed for harvesting the channelled systems. The conveyor transports the cut stalks to the berm behind the harvester.

The fourth and fifth channels of Systems III and IV were harvested on July 16, 1981. The first three channels of these same systems were later harvested on August 26, 1981. Harvesting was carried out on these dates to compare the amounts of nutrients removed and the extent and quality of regrowth occurring. Special sampling was also conducted in an attempt to assess the effect of harvesting on effluent quality. The harvested cattails were weighed and sampled for nutrient and heavy metal analyses.

5.0 RESULTS AND DISCUSSION

Although general comments will be made in this and the following sections, which may address anyone, or all of the marsh systems, detailed assessments will only be made of Systems II, III, IV and V. The complexity of System I makes any interim assessment of its operation very difficult in this, its first year of operation.

It should be noted that for purposes of this paper, gross assessments of only the more conventional parameters have been made. The complexity of operating variables during this initial phase of operation of the marsh, make the results to date quite preliminary in nature. Further long term studies are required to confirm the conclusions drawn.

Flows for this paper have been estimated from bucket discharge readings rather than digitized flow records. However, since these readings were normally taken in the first half of the day, outflow volumes will be overestimated since the readings will not have been influenced by afternoon evapotranspiration. Consequently, any calculated removal efficiencies are on the conservative side.

Data are presented both in concentrations and mass loadings, however, in determining removal efficiencies, mass values rather than concentrations have been used. Rainfall and evapotranspiration within the relatively large surface areas of the marshes significantly affected outflow volumes, which ranged from as high as 160% to as low as 30% of the influent volumes on any particular day.

Although influent and effluent concentrations have been presented in tables on the basis of monthly averages of weekly values, mass loadings and removal efficiencies were calculated on a period basis. As mentioned in Section 4.0, the operation program to date has involved four distinct flow regimes. These flow regimes were used as the basis for selection of the four study periods and Table 1 provides pertinent identification of each. Period 2 has been divided into Period 2A and Period 2B on the basis of temperature, with 2A occurring at the severest time of the year.

As previously mentioned, Systems I, II and III are fed from the east lagoon, while Systems IV and V receive aeration cell effluent¹. The quality of the feed to Systems I, II and III is presented in Table 2, while that to Systems IV and V is given in Table 3. Effluent concentrations of the same parameters from Systems II to V are presented in Tables 4 to 7, respectively.

Tables 8 to 11 present influent and effluent mass loadings as well as percent removals for selected parameters for the four flow periods for System II to V.

These tables are discussed in the following sections.

5.1 Temperature

Average influent temperatures for each period are presented in Table 1. Summer temperatures were quite similar in both feed streams with a single day high in August of 26°C. Winter temperatures

¹ note: From this point on, the feed stream from the aeration cell will be termed aeration cell influent while that from the lagoon will be termed lagoon influent.

in the aeration cell influent were, however, consistently several degrees higher than were those of the lagoon influent as would be expected. January temperatures of the lagoon influent hovered just above 0°C while the minimum recorded temperature of the aeration cell influent was 3.5°C .

Temperatures of all marsh effluents were very similar and closely followed those of the lagoon influent and measured as 0°C for most of January.

5.2 Dissolved Oxygen

Dissolved oxygen concentrations in the lagoon influent have not followed the classical seasonal trends of summer high and winter low values. This is likely because of the location of the pump inlet which is at the bottom of the lagoon where, except for periods of extensive algae blooms, or at times of wind-caused turnover, DO values would be expected to be, and indeed were, very low. Throughout June and July, 1981 (data not presented), the lagoon influent rarely contained any measurable DO, while during October and November, 1980 it frequently exceeded 10 mg/l. Dissolved oxygen values fluctuated between 0 and 3 mg/l throughout the winter. The pump inlet was situated at the bottom of the lagoon to eliminate any winter freezing problems and because the lagoon contents are drawn down in the spring. It is intended that a floating inlet structure be constructed for use in subsequent summers.

Low summertime DO levels close to 0 mg/L in the aeration cell influent reflect the insufficient capacity of the existing aeration equipment during peak summer loading periods. Even during the winter period, DO levels in this feed stream seldom exceeded 3 mg/l.

All experimental marsh systems initially followed classical seasonal DO trends with high values in the fall and winter values ranging between 0 and 7 mg/l. The winter values of the channelled Systems III and IV were slightly higher than the open marsh Systems II and V, no doubt reflecting the oxygen contribution from the air blower which was used to prevent freezing in the channelled marsh connecting culverts. Total anoxia occurred in Systems II and V for a short period in late January. Anoxic conditions occurred again during the latter part of June, all of July and most of August in Systems II and V and from mid-July into early August in Systems III and IV. The latter conditions can be attributed in part to the extremely dense layer of duckweed which developed on the surfaces of all marsh systems during the summer of 1981 and the sludge mats which formed on the inlet ends of Systems IV and V (see Section 5.4). Also, the high evapotranspiration rates during July and August and short-circuiting, especially in the open marshes, caused by the dense cattail growth, probably led to stagnant areas and severe anaerobic conditions. This condition is very significant when assessing treatment efficiencies later in this paper.

5.3 Five-Day Biochemical Oxygen Demand (BOD)

The aeration cell influent feed was characterized by highly variable BOD concentrations which frequently exceeded 100 mg/l as shown in Figure 2. This variability was significantly attenuated during passage of the wastewater through Systems IV and V. Effluent values were consistently below 5 mg/l during the fall of 1980 but increased to as high as 30 in January/February. Except for one odd value on June 2, 1981, System IV consistently outperformed that of open System V.

Figure 4 presents a graph of percent BOD removal in each of the systems for the four study periods. This figure also reflects the improved performance of the channeled systems. Other than the low value of System II during the winter, significant BOD reductions were realized in all systems; the higher reductions of Systems IV and V being no doubt due to the higher influent concentrations of their feed stream.

5.4 Suspended Solids (SS)

Graphs of weekly SS data for the influent and effluents of Systems IV and V are presented in Figure 5 and those for Systems II and III in Figure 6. As with BOD, SS concentrations in the aeration cell influent were quite high and variable but followed a seasonal trend with low values during the winter/spring period. This was also the period of alum addition to the raw sewage for phosphorus removal purposes, but this should not have reduced aeration cell solids levels. Reduced biological activity under cold conditions and weaker strength sewage, may have been the causes.

The high solids loadings to Systems IV and V resulted in the development of dense sludge mats at the influent ends of these marshes. By springtime, considerable dieback of Typha spp. had occurred in the sludge mat areas and some hydrogen sulphide production was noticed. Recovery of the cattails continued throughout the summer period.

Effluent SS concentrations in Systems IV and V were generally less than 15 mg/l although some higher values occurred in June/July, especially in System V.

Concentrations of SS in the influents to Systems II and III were generally less than 25 mg/l except for peaks in the late spring/summer period. These peaks coincided with phytoplankton blooms in the facultative lagoon when chlorophyll concentrations approached 200 µg/L.

Effluent SS concentrations in the two systems were similar with some deterioration in quality, again particularly in the open marsh (System II), occurring in the summer period.

Trends in SS percent removals for the four study periods are presented in Figure 7. Again, the channelled marshes outperformed the open marshes although both Systems II and III experienced low percent removal values during Periods 2 and 3.

5.5 Phosphorus (P)

Weekly values of Total Phosphorus (TP) concentrations in the influents and effluents of the marshes are shown in Figures 8 and 9. Concentrations generally ranged between 2 and 6 mg/l in the aeration cell influent and 1 and 2 mg/l in the lagoon influent. As mentioned, chemical addition for phosphorus removal is practiced from September to May and consequently, the phosphorus level within the lagoon was lower during this period (except again for one odd value on April 14). The similarly lower values in the aeration cell influent during this period probably reflect weaker sewage strengths during the winter period.

Effluent TP concentrations of all systems tended to follow expected seasonal trends with peak values occurring in the colder winter months, however, all values began increasing again in June. In fact, for a short period in August, 1981 there was a net loss in TP from System II. System IV was the only system which provided a relatively consistent effluent with respect to TP concentration.

The poor performance of Systems II, III and V in the summer/fall of 1981 may be explained by the discussions regarding DO in Section 4.2. Anoxic conditions undoubtedly led to the release of phosphorus which had been bound in the marshes. Aeration tubing was installed along the length of the final channel of System IV during July and August, 1981 on an experimental basis and although no measurable DO level was achieved, perhaps adequate conditions were provided to prevent the release of phosphorus evident in the other systems.

Soluble Reactive Phosphorus (SRP) concentrations in all system influents and effluents are presented in Figures 10 and 11. Of note in both influents, is the decrease in SRP concentration during the chemical addition period, indicating the effective precipitation of soluble phosphorus.

Percent removals of TP and SRP are presented in Figures 12 and 13, respectively. Again, the high removals of both TP and SRP in Period 1 dropped off considerably during the winter period for all systems, although the higher removals of TP in Systems IV and V are undoubtedly due to the precipitation in the marshes of chemically bound phosphorus. System V showed negative reductions of SRP in both the winter and spring periods of Period 2, while removals of both TP and SRP dropped off again in System II and to a lesser extent in System V during Period 4.

Once again, the channelled marshes outperformed the open marshes with respect to both Total and Soluble Reactive Phosphorus.

5.6 Nitrogen (N)

Total Nitrogen (TN) concentrations in the aeration cell influent fluctuated between 10 and 37 mg/l and showed little seasonal trend (Figure 14). Although less variation occurred in the lagoon influent (Figure 15), peaks occurred in January, April and July.

Total Nitrogen concentrations in the effluents of all four experimental marshes were remarkably similar and generally followed influent concentration trends until the late summer, 1981 period. At this time, TN concentrations in the effluents of the two open marshes (Systems II and V) increased significantly.

Nitrites and Nitrates comprised an insignificant portion of the Total Nitrogen of both influents and effluents of all systems (Tables 2 to 7).

Ammonia concentrations, on the other hand, comprised a significant percentage of the Total Nitrogen in the two influent streams (Tables 2 to 7) and were similar in both although slightly lower in the lagoon influent, reaching a minimum average value of 1.4 mg/l for May. As with TN, Ammonia concentrations in all marsh effluents were very low (<1 mg/l) during the fall/early winter of 1980, increased considerably during the winter period, decreased again in early summer and once more increased in late summer, 1981.

Again, the effluent Ammonia concentrations were consistently lower in the effluents from the channelled marshes than the open marshes.

As can be seen from Figures 16 and 17, both Total and Ammonia Nitrogen removals followed similar patterns to the other parameters.

6.0 GENERAL OBSERVATIONS

The following observations of specific and general aspects of the operation of the study facility provide an insight into the treatment which may be expected from an artificial marsh of this nature, and may be used to help clarify some of the tentative conclusions which have been drawn from the preliminary phase of this study.

6.1 System Configuration

The data collected to date on the artificial marsh systems demonstrate the superior performance of the channelled marsh over the open marsh of equal surface area. It would appear that this superior performance is due to the greater use of the total marsh volume, the channels reducing the degree of short-circuiting and resulting in reduced loadings on subsequent channels, leading to higher effluent quality.

The ideal marsh system would ensure uniform flow across the full surface area of the marsh as well as providing for continuous movement of the liquid in the marsh. Even distribution of the influent feed across the marsh is essential and may best be accomplished by the use of perforated irrigation pipe across the influent end of the marsh. Perhaps intermittent baffles along the length of the marsh could be used to improve circulation within the marsh and reduce short-circuiting.

6.2 Retention Time

Although not readily visible because of the manner in which the data have been presented, retention time seems to have a strong influence on effluent quality; with effluent quality deteriorating

at both too short and too lengthy a retention period. Best treatment results coincide with retention times of between 7 and 10 days, achieved in the fall of 1980 and early summer of 1981.

The shortest retention time occurred in the coldest period of the year (Table 1) when the entire facility was ice and snow covered and treatment efficiency would have been expected to be low. The retention time during mid-summer was also low because of the profuse cattail growth and the higher efficiencies of the early summer period quickly deteriorated. Treatment picked up again in the early fall as flows were reduced but dropped off again as retention periods became too long (≈ 18 days) due to high rates of evapotranspiration. The long retention period leads to stagnation and subsequent anoxia with the potential release of bound Nitrogen and Phosphorus.

When establishing flow rates and retention times, one must consider many factors other than marsh area and depth. Other factors include cattail growth, ice layer in winter, rainfall and evapotranspiration.

6.3 Pretreatment

Problems experienced with the operation of the artificial marsh systems fed with aeration cell influent appear to have been caused by its high suspended solids content. These formed sludge mats at the influent ends of the marshes killing back the vegetation and leading to hydrogen sulphide formation. The higher loadings of BOD, Phosphorus and Nitrogen appeared to have little adverse effect on effluent quality.

For artificial marshes it is therefore suggested that the minimum form of pretreatment include solids removal by clarification to the equivalent of primary effluent quality.

6.4 Harvesting

Harvesting of different channels of Systems III and IV was carried out on July 16 and on August 26, at which times the cattails averaged approximately 3 and 3.2 meters in height, respectively. The mass of cattails and associated Nitrogen and Phosphorus removed are given below:

<u>Harvest Date</u>	<u>Dry Weight</u> (kg/channel)	<u>Mass Removed</u>	
		N	P
		(kg/ha)	
July 16, 1981	86	150	17
August 26, 1981	209	366	42

As can be seen, the August harvest removed over twice the amount of material than did the July harvest although each removed a significant amount of nutrients. Using the August harvesting data and comparing the mass of Nitrogen and Phosphorus removed to the mass fed to System III in the lagoon influent, it can be calculated that the August harvest removed the equivalent of 70 days loading of Nitrogen and 84 days loading of Phosphorus.

The common cattail, Typha spp. has been found to be an ideal vegetation for use in artificial marshlands for sewage effluent treatment. The Listowel marshes were planted with cattail shoots collected from local ditch areas, which adapted well to the sewage environment reaching heights considerably in excess to native growths. When harvested, the cattails removed a significant amount of nutrients and regrowth was exceptional, with the cattails regrowing at the rate of about 12 cm per week.

No estimation can be made at this time, of the effect of harvesting on marsh effluent quality. However, in view of the rapid rate of regrowth and substantial quantities of nutrients removed, it is anticipated that harvesting would have an immediate and overall positive impact on the marsh performance.

Marsh performance may be further improved by the harvesting of cattails twice per year. An early summer cut would remove lesser amounts of biomass but would stimulate rapid growth. A second cut in late summer or early fall would remove the summer's biomass and contained nutrients prior to plant senescence in late fall.

6.5 Bacterial Reduction

As mentioned, the raw sewage entering the Town of Listowel's wastewater treatment facility contains a significant contribution of flow from a local food (primarily poultry) processing industry. Consequently, the sewage contains exceptionally high levels of fecal coliforms, fecal streptococci and salmonella bacteria, particularly during the winter months.

Figures 18 and 19 present graphs of influent and effluent fecal coliforms and fecal streptococci for each of the five systems. As illustrated, considerable reductions in both forms of bacteria were evident in all marsh systems in the fall and spring periods. Treatment efficiency, however, decreased significantly during the winter, especially in the open marsh systems.

In general, the bacterial quality of the marsh outflows was comparable to the quality of disinfected secondary effluent except during the winter months. Again, the channelled marshes (Systems II and IV) exhibited superior treatment to the open marshes, especially throughout the winter months.

Although salmonella were characteristically recovered from the aeration cell and lagoon influents, the organism was only very infrequently found in the effluents of Systems II, III and IV.

6.6 Cost of the Artificial Marsh System

The total engineering and construction cost of the Listowel Artificial Marsh System was approximately \$284,000. This cost, however, included many items and specifications specifically for research purposes. For example, the bottoms of the marsh systems were levelled by a laser to within ± 2.5 cm; influent and effluent flow control and measuring stations were established for all marshes; a lined control marsh was provided; and observation wells for ground-water monitoring were provided.

Subtracting out those costs incurred solely for research and specific monitoring purposes, it is estimated that the capital costs of a channelled marsh system to treat a flow of $4545 \text{ m}^3/\text{day}$ would cost approximately \$400,000 exclusive of land costs. Operational costs would be minimal requiring little more than pump maintenance and once per year harvesting.

7.0 CONCLUSIONS

Preliminary water quality data from the Listowel Artificial Marsh suggest that artificial marshes have the capacity to significantly improve the quality of partially treated wastewaters. Although a much longer study period is required to assess long-term performance, and to establish optimal design and operational criteria, the following conclusions can be drawn from the study to date:

- a) As evidenced by the rapid growth of the cattail Typha spp. following initial planting, the common cattail is well adapted to the sewage environment. Regrowth rates and the density and height of growth attained confirm this.
- b) System configuration is very important with channelled marshes providing superior treatment to open marshes. Even distribution of the influent sewage flow is essential, along with continuous flow across the entire surface area of the marsh to eliminate short-circuiting and formation of stagnant areas.
- c) Retention time of the sewage within the marsh is also critical, with too low a retention time decreasing treatment efficiency due to insufficient contact, and too lengthy a retention time leading to stagnation and anoxic conditions. This study to date would suggest an optimum retention period of from 7 to 10 days at an operating depth of about 20 cm.
- d) The artificial marsh is capable of accepting, and improving the quality of both partially treated sewage and sewage of secondary quality. While effluent quality of the marsh is partially dependent upon influent quality, treatment efficiency appears to be more dependent upon such factors as retention time, degree of short-circuiting and stagnation, temperature and flow rate than actual mass loading. High levels of suspended solids can lead to sludge accumulation with resultant reduced treatment and should be removed prior to the marsh.

- e) The artificial marsh appears capable of reducing bacterial levels in sewage effluent to the equivalent of disinfected secondary effluent except perhaps during the coldest winter months.
- f) Reduced winter performance was no doubt partly influenced by the high hydraulic loadings and short retention times. Additional information, at reduced flows with concomitant longer retention times, is required to properly assess the winter capabilities of the artificial marsh process. Even so, System III, the channelled marsh treating lagoon influent, achieved BOD, TP and TN reductions of 56, 35 and 25%, respectively, during the 1980/1981 winter period. Similarly, System IV treating aeration cell influent achieved BOD, TP and TN reductions of 79, 71 and 30%, respectively, for the same period.
- g) Harvesting of cattails is a potential marsh management option and it is suggested that two harvestings be carried out per year. An early summer harvest will stimulate rapid cattail growth, and one in early fall will remove the summer's biomass and significant amounts of nitrogen and phosphorus from the system.

TABLE 1

Characteristics Of Study Period

Period	Dates	Influent Temp. (°C)	Depth (cm)	Average Flow (m ³ /day)	Nominal Retention (days)	Calculated Retention (days)
1	July 14-Dec. 6					
	System II	12.9	14	18.2	7.07	6.4
	III	12.9	14	17.7	7.95	7.2
	IV	17.5	14	16.5	8.54	7.5
	V	17.5	14	18.0	7.16	6.5
2A	Dec. 7-Feb. 28					
	System II	1.6	28	65.9	4.0	2.0
	III	1.6	28	67.4	4.6	2.3
	IV	6.4	28	51.6	6.0	3.0
	V	6.4	28	54.5	4.8	2.4
2B	March 1-April 30					
	System II	7.7	28	77.3	3.4	2.8
	III	7.7	28	79.7	3.9	3.4
	IV	10.2	28	49.9	6.2	5.2
	V	10.2	28	52.6	5.0	4.3
3	May 1-July 24					
	System II	19.7	20	33.3	5.6	4.0
	III	19.7	20	38.2	5.5	3.8
	IV	19.4	20	32.3	6.5	4.4
	V	19.4	20	28.1	6.6	4.6
4	July 25-Sept. 1					
	System II	23.0	20	17.5	10.6	13.3
	III	23.0	20	16.6	12.6	18.9
	IV	21.5	20	18.2	11.5	18.9
	V	21.5	20	17.6	10.6	16.3

* Calculated value considers volume reduction due to cattail growth and ice layer during winter, rainfall, evapo-transpiration and limited dye tracer data.

TABLE 2

Lagoon Influent Quality - Feed to Systems I, II and III
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD ₅	SS	TP	SRP	TKN	NO ₂ +NO ₃	NH ₃
mg/l							
Aug., 1980	11	22	1.9	1.6	12	0.4	6.7
Sept.	18	23	1.8	1.3	8	1.0	3.4
Oct.	11	8.4	1.1	0.7	8	0.4	3.9
Nov.	12	9.7	0.9	0.4	9	0.3	4.7
Dec.	14	23	0.8	0.3	10	0.3	5.2
Jan., 1981	25	15	1.0	0.5	14	<0.01	9.4
Feb.	33	18	1.1	0.7	15	<0.01	10.1
Mar.	27	14	1.0	0.24	12	<0.01	7.3
April	29	63	0.9	0.16	14	0.12	5.6
May	42	36	1.1	0.15	10	0.06	1.4
June	26	29	1.6	0.85	16	0.03	8.8
July	13	18	1.9	1.26	16	0.03	11.3
Aug.	12	18	2.2	1.52	14	0.15	9.7

TABLE 3

Aeration Cell Influent Quality - Feed to Systems IV and V
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD ₅	SS	TP	SRP	TKN	NO ₂ +NO ₃	NH ₃
mg/l							
Aug., 1980	39	80	2.3	2.55	19	1.35	10.4
Sept.	64	182	3.7	0.35	21	0.68	7.3
Oct.	52	190	4.9	0.09	24	0.32	7.9
Nov.	97	189	4.7	0.07	23	0.02	4.9
Dec.	68	59	2.4	0.16	15	0.01	5.2
Jan., 1981	72	88	3.2	0.16	24	<0.01	11.0
Feb.	91	46	1.9	0.13	13	<0.01	7.5
Mar.	53	56	2.8	0.31	15	<0.01	6.0
April	38	54	1.9	0.16	16	0.01	7.1
May	90	160	5.0	0.90	28	0.01	8.2
June	105	221	6.8	1.20	29	<0.01	9.3
July	56	162	5.1	1.47	25	<0.01	12.2
Aug.	26	66	3.7	2.25	20	0.45	14.3

TABLE 4

Marsh System II Effluent Characteristics
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD	SS	TP	SRP	TKN	NO ₂ +NO ₃	NH ₃
mg/l							
Aug., 1980	17	90	0.58	0.47	3.1	0.26	0.83
Sept.	5	10	0.29	0.19	2.9	0.01	0.3
Oct.	2	1	0.10	0.07	1.47	0.18	0.006
Nov.	5	5	0.16	0.07	1.89	1.16	0.013
Dec.	11	24	0.46	0.18	6.65	0.53	3.16
Jan., 1981	20	14	0.93	0.50	13.3	0.01	9.0
Feb.	32	14	0.96	0.38	13.0	0.06	7.4
Mar.	23	10	0.69	0.33	9.1	0.02	6.2
April	17	19	0.52	0.08	7.4	0.21	4.0
May	5	10	0.49	0.18	5.3	0.04	0.56
June	13	18	0.75	0.36	9.4	0	4.82
July	24	43	1.14	0.33	14.2	0	8.4
Aug.	9	7	2.42	2.58	13.0	0.01	11.1

TABLE 5

Marsh System III Effluent Characteristics
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD	SS	TP	SRP	ZKN	NO ₂ +NO ₃	NH ₃
mg/L							
August 1980	8	13	0.55	0.31	5.3	0.29	0.33
Sept.	5	11	0.18	0.09	2.7	0.02	0.20
Oct.	1.4	2	0.10	0.09	1.4	0.01	0.01
Nov.	2.4	3	0.12	0.07	1.6	0.98	0.02
Dec.	8	11	0.43	0.16	5.9	0.63	2.60
Jan. 1981	9.2	10	0.70	0.41	12.6	0.06	6.68
Feb.	15	19	0.84	0.42	12.1	0.02	7.47
March	12	9	0.52	0.39	8.9	0.01	6.62
April	18	24	0.60	0.10	7.3	0.30	2.9
May	6	8	0.27	0.14	4.7	0.02	0.28
June	10	14	0.41	0.19	7.1	0	4.27
July	16	31	0.79	0.18	12.1	0	6.72
August	10	10	1.02	0.68	7.8	0.01	4.12

TABLE 6

Marsh System IV Effluent Characteristics
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD	SS	TP	SRP mg/L	TKN	NO ₂ +NO ₃	NH ₃
August 1980	-	-	-	-	-	-	-
Sept.	2.8	5.2	0.06	0.04	1.4	0.16	0.10
Oct.	1.8	1.1	0.05	0.02	1.3	1.02	0.19
Nov.	3.2	4.4	0.11	0.03	1.5	1.46	0.07
Dec.	15	3.6	0.51	0.08	8.0	0.24	4.4
Jan. 1981	22	9	0.92	0.31	16.7	0.02	11.7
Feb.	10	7	0.67	0.34	10.4	0.01	6.2
March	18	12	0.80	0.30	9.5	0.01	5.4
April	9	8	0.45	0.13	7.3	0.10	2.3
May	14	14	0.67	0.30	7.8	0.07	1.9
June	34	34	1.81	0.65	15.0	0	7.9
July	9	9.1	0.97	0.53	11.9	0	8.8
August	9	7	0.52	0.33	7.5	0.01	5.5

TABLE 7

Marsh System V Effluent Characteristics
(Monthly Averages Based Upon Weekly Grab Samples)

Date	BOD	SS	TP	SRP mg/L	TKN	NO ₂ +NO ₃	NH ₃
August 1980	2.4	9	0.22	0.16	2.8	0.29	0.24
Sept.	2.6	5	0.12	0.09	1.7	0.03	0.27
Oct.	2.2	1	0.08	0.02	1.5	0.74	0.22
Nov.	4.8	6	0.21	0.03	2.9	0.33	0.67
Dec.	15	5	0.61	0.12	9.0	0.44	5.1
Jan. 1981	25	13	1.19	0.17	17.9	0.03	6.4
Feb.	18	12	0.87	0.30	11.2	0.42	5.9
March	26	13	1.02	0.43	10.0	0.01	4.4
April	12	9	0.65	0.11	10.2	0.04	4.2
May	36	20	0.94	0.31	13.3	0.01	1.6
June	35	31	1.61	0.82	16.2	0	8.3
July	29	7	2.03	0.84	23.3	0	13.1
August	8	8	2.50	2.22	15.5	0.01	15.5

TABLE 8

Mass Loadings* And Percent Reductions - System II

	BOD	SS	TP	SRP	TN	NH ₃
Period 1						
Influent	237	292	25.5	18	179	86
Effluent	41	84	2.7	2	40	0.7
% Reduction	83	71	89	89	78	99
Period 2A						
Influent	1581	1252	63	34	857	540
Effluent	1477	1125	55	25	780	457
% Reduction	7	10	13	26	9	15
Period 2B						
Influent	2319	1237	85	38	1082	672
Effluent	1516	1137	45	15	621	386
% Reduction	35	8	47	60	43	42
Period 3						
Influent	899	932	50	17	466	240
Effluent	576	875	29	10	359	179
% Reduction	36	6	42	41	23	25
Period 4						
Influent	210	316	39	27	245	170
Effluent	120	93	32.2	28	173	148
% Reduction	43	70	17	neg.	29	13

* Mass Loadings are in grams/day.
To convert to kg/ha/day multiply by 10^{-2} .

TABLE 9

Mass Loadings* And Percent Reductions - System III

	BOD	SS	TP	SRP	TN	NH ₃
Period 1						
Influent	230	292	25.5	18.2	179	86
Effluent	35	52	1.7	1.2	25	0.7
% Reduction	85	82	93	94	86	99
Period 2A						
Influent	1618	1281	65	34	876	552
Effluent	705	833	42	21	654	359
% Reduction	56	35	35	38	25	35
Period 2B						
Influent	2391	1275	88	39	1116	693
Effluent	1024	1093	38	17	553	328
% Reduction	57	14	57	56	50	53
Period 3						
Influent	1031	1070	57	19	535	275
Effluent	397	639	18	6	288	143
% Reduction	61	40	68	68	46	48
Period 4						
Influent	199	299	37	25	232	161
Effluent	111	111	11	6	86	46
% Reduction	44	63	70	76	63	71

* Mass Loadings are in grams/day.
To convert to kg/ha/day multiply by 10^{-2} .

TABLE 10

Mass Loadings* And Percent Reductions - System IV

	BOD	SS	TP	SRP	TN	NH ₃
Period 1						
Influent	1040	2640	64	12.5	363	125
Effluent	31	41	0.8	0.4	25	1.5
% Reduction	97	98	99	97	93	99
Period 2A						
Influent	3973	3302	129	8	877	408
Effluent	844	317	37	13	617	390
% Reduction	79	90	71	neg.	30	4
Period 2B						
Influent	2246	2745	140	12	798	324
Effluent	577	412	26	9	346	160
% Reduction	74	85	81	25	57	51
Period 3						
Influent	2713	5846	181	38.4	872	320
Effluent	599	602	37	15.1	346	201
% Reduction	78	90	80	62	60	39
Period 4						
Influent	474	1204	68	41	364	260
Effluent	99	77	6	3	83	61
% Reduction	79	94	91	92	77	76

* Mass Loading are in grams/day.
To convert to kg/ha/day multiply by 10^{-2} .

TABLE 11

Mass Loading* And Percent Reductions - System V

	BOD	SS	TP	SRP	TN	NH ₃
Period 1						
Influent	1134	2880	70	13.6	396	137
Effluent	48	63	2	0.6	38.5	5
% Reduction	96	8	98	95	90	96
Period 2A						
Influent	4197	3488	136	8.2	926	430
Effluent	1010	532	47	10	676	308
% Reduction	76	85	65	neg.	27	28
Period 2B						
Influent	2452	2998	153	13	872	354
Effluent	940	544	41	13	500	213
% Reduction	62	82	73	0	43	40
Period 3						
Influent	2360	5086	157	33.4	759	278
Effluent	975	1287	46	17.4	521	240
% Reduction	59	75	71	48	31	14
Period 4						
Influent	458	1162	65	40	352	252
Effluent	91	91	28	23	177	177
% Reduction	80	92	56	42	50	30

* Mass Loading are in grams/day.
To convert to kg/ha/day multiply by 10⁻².

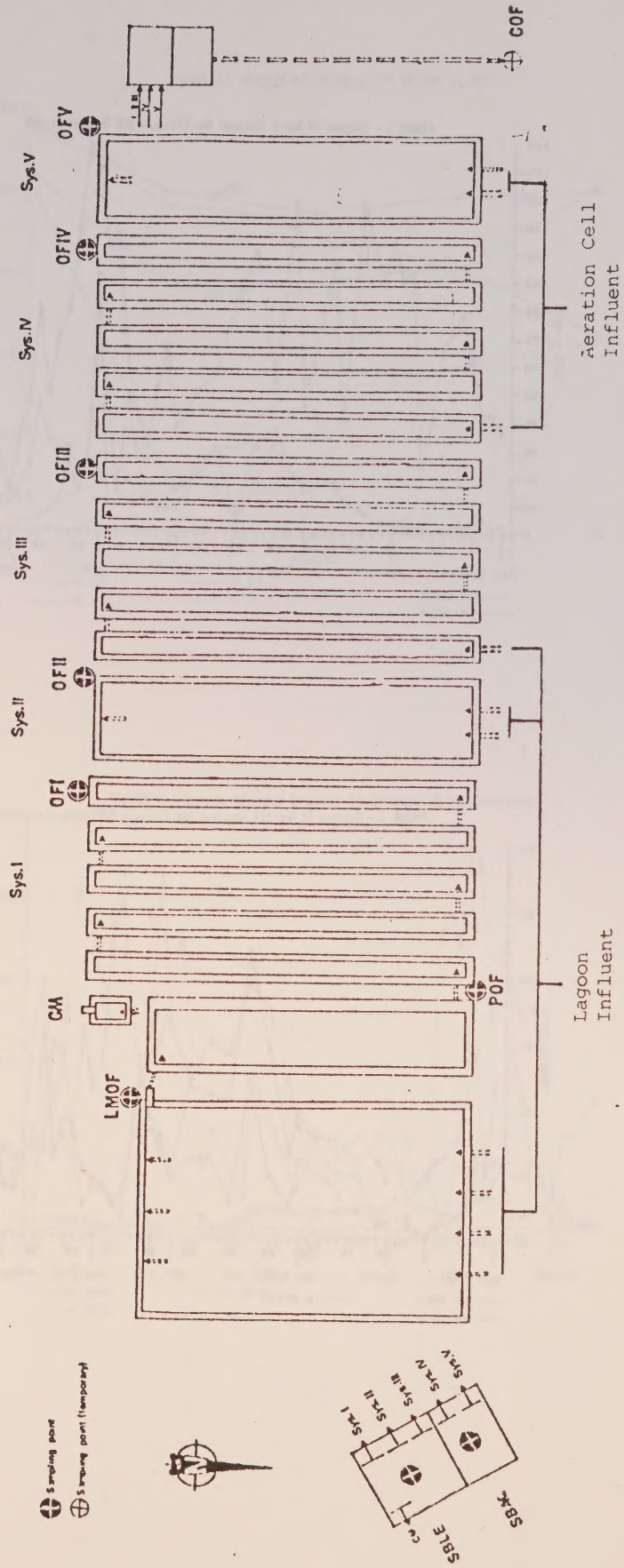


FIGURE 1 - LISTOWEL ARTIFICIAL MARSH FACILITY

FIGURE 2 - SYSTEMS IV AND V INFLUENT AND EFFLUENT BOD CONCENTRATIONS

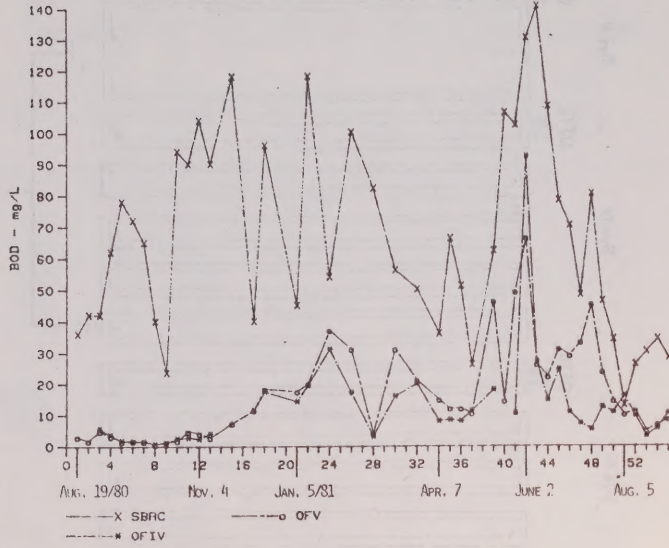


FIGURE 3 - SYSTEMS II AND III INFLUENT AND EFFLUENT BOD CONCENTRATIONS

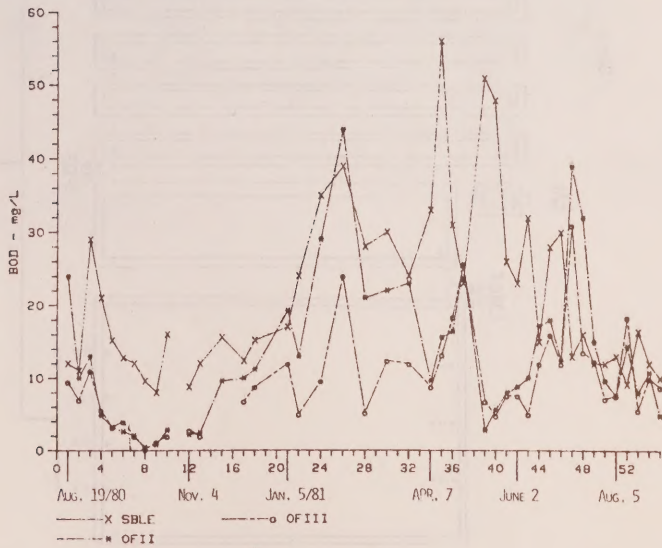


FIGURE 4 - PERCENT BOD REMOVALS FOR SYSTEMS II TO V

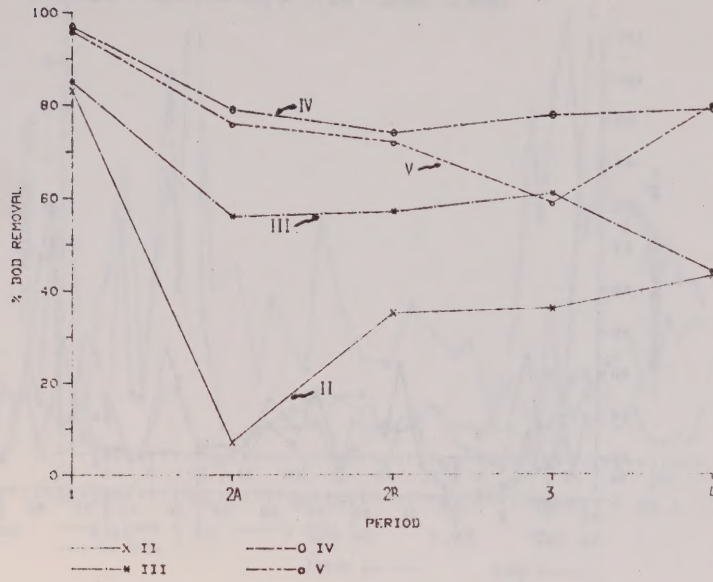


FIGURE 5 - SYSTEMS IV AND V INFLUENT AND EFFLUENT SS CONCENTRATIONS

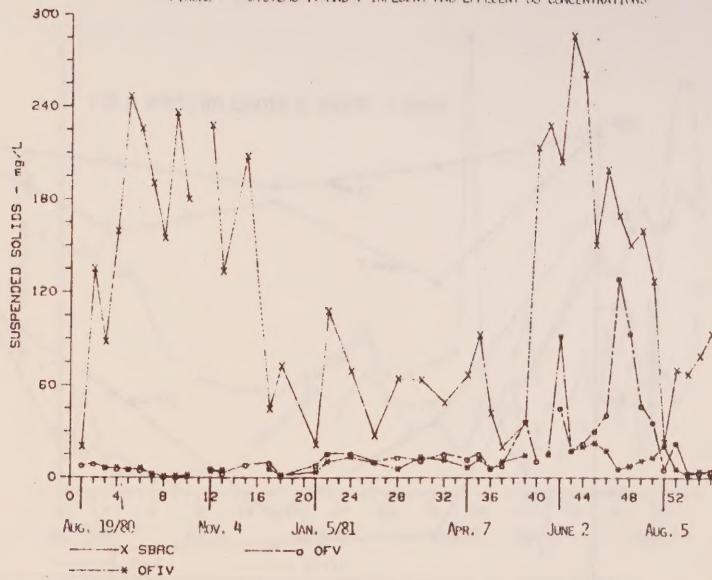


FIGURE 6 - SYSTEMS II AND III INFLUENT AND EFFLUENT SS CONCENTRATIONS

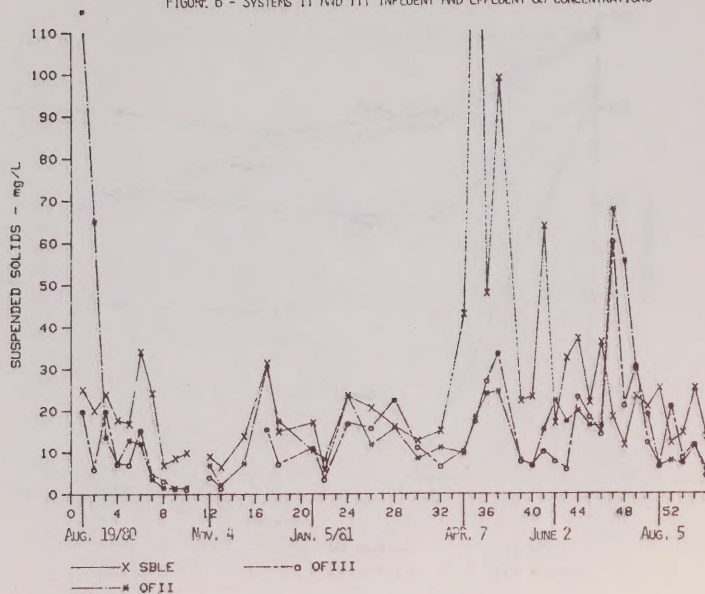


FIGURE 7 - PERCENT SS REMOVALS FOR SYSTEMS II TO V

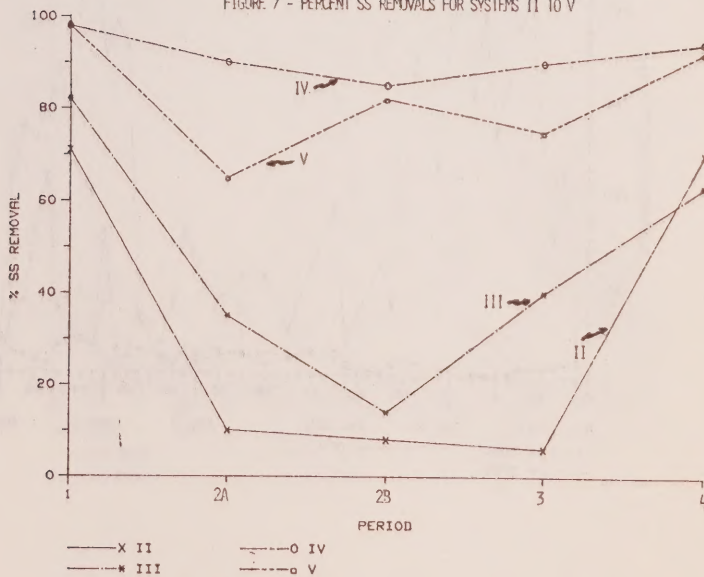


FIGURE 8 - SYSTEMS IV AND V INFLUENT AND EFFLUENT TP CONCENTRATIONS

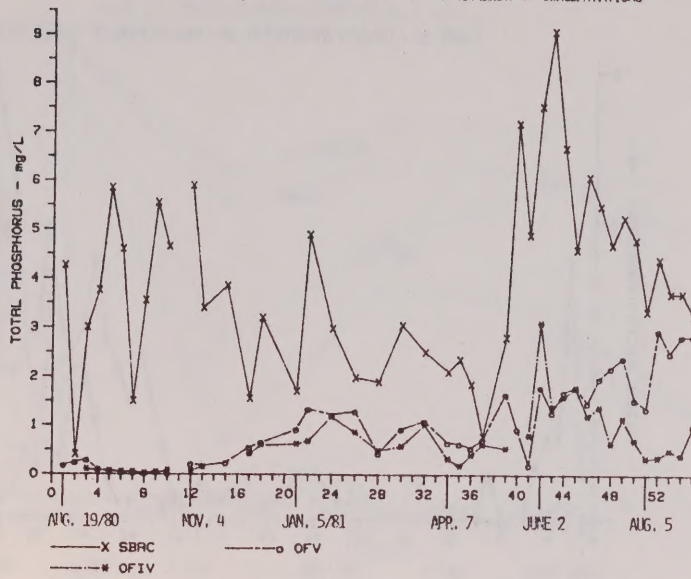


FIGURE 9 - SYSTEMS II AND III INFLUENT AND EFFLUENT TP CONCENTRATIONS

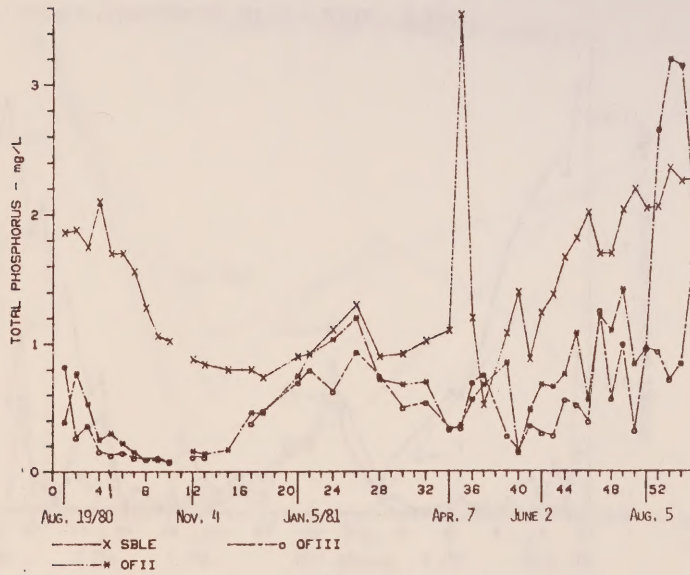


FIGURE 10 - INFLUENT AND EFFLUENT SRP CONCENTRATIONS OF SYSTEMS IV & V

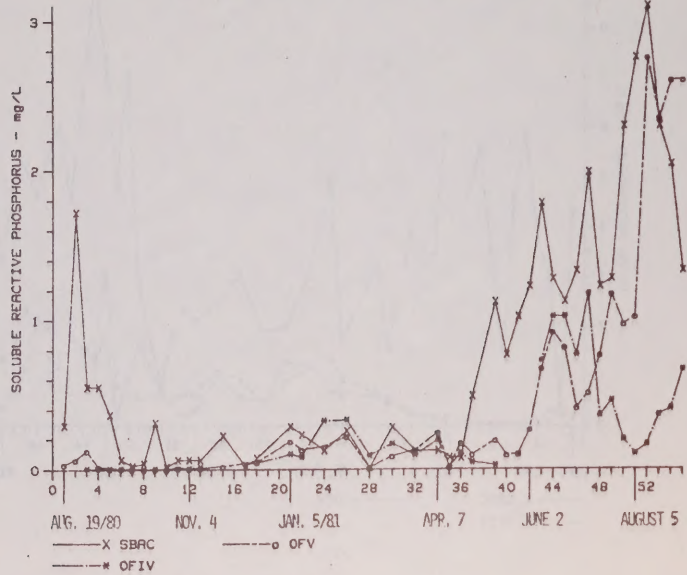


FIGURE 11 - INFLUENT & EFFLUENT SRP CONCENTRATIONS OF SYSTEMS II & III

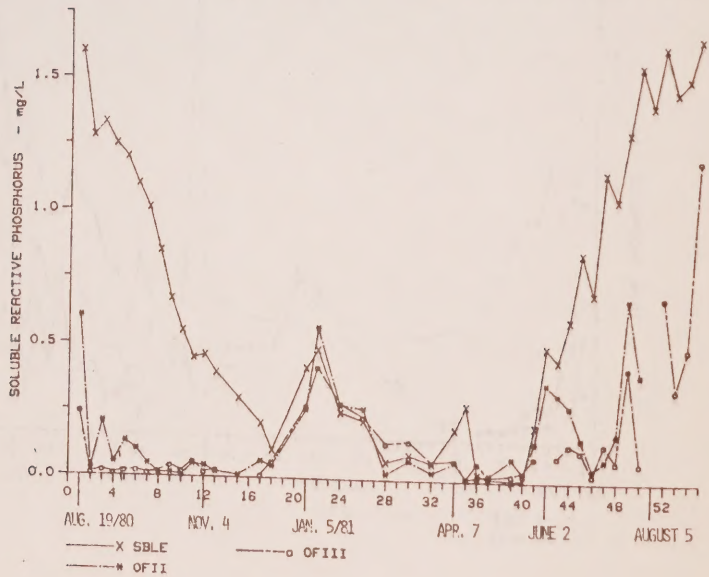


FIGURE 12 - PERCENT TP REMOVALS FOR SYSTEMS II TO V

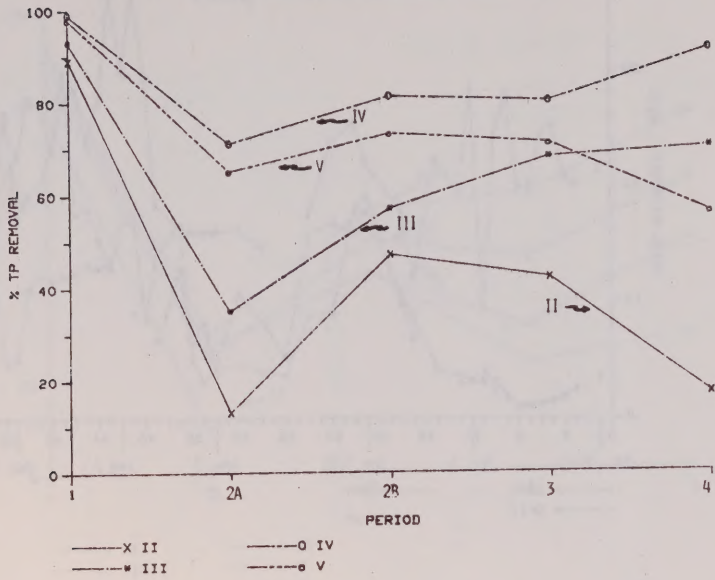


FIGURE 13 - PERCENT SRP REMOVALS FOR SYSTEMS II TO V

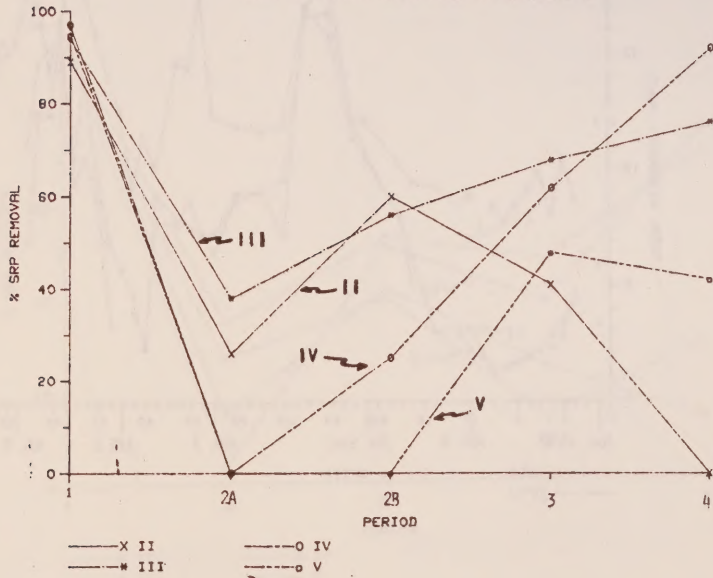


FIGURE 14- SYSTEMS IV AND V INFLUENT AND EFFLUENT TN CONCENTRATIONS

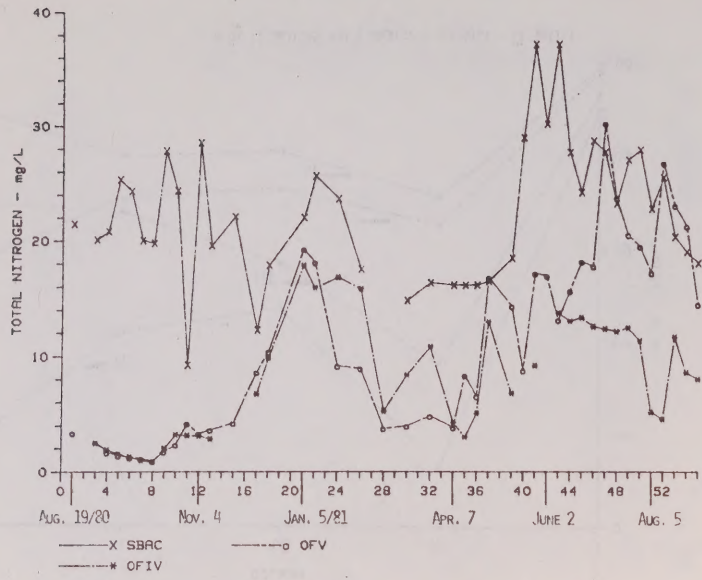


FIGURE 15 - SYSTEMS II AND III INFLUENT AND EFFLUENT TN CONCENTRATIONS

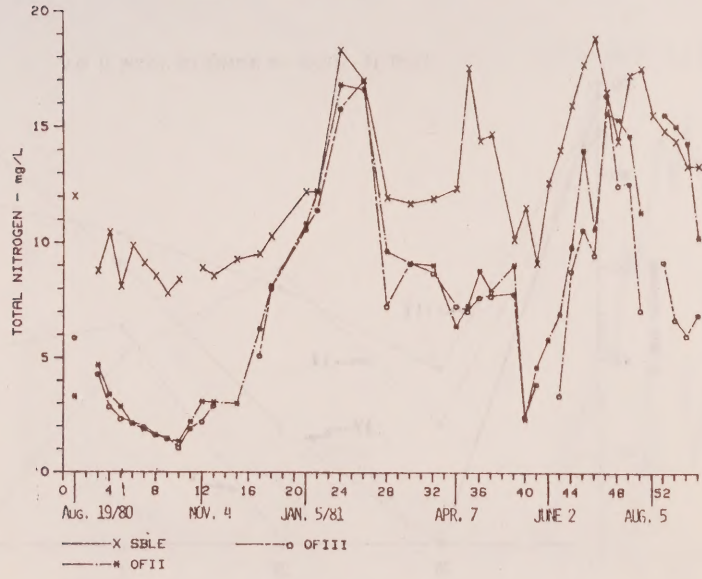


FIGURE 16 - PERCENT TN REMOVALS FOR SYSTEMS II TO V

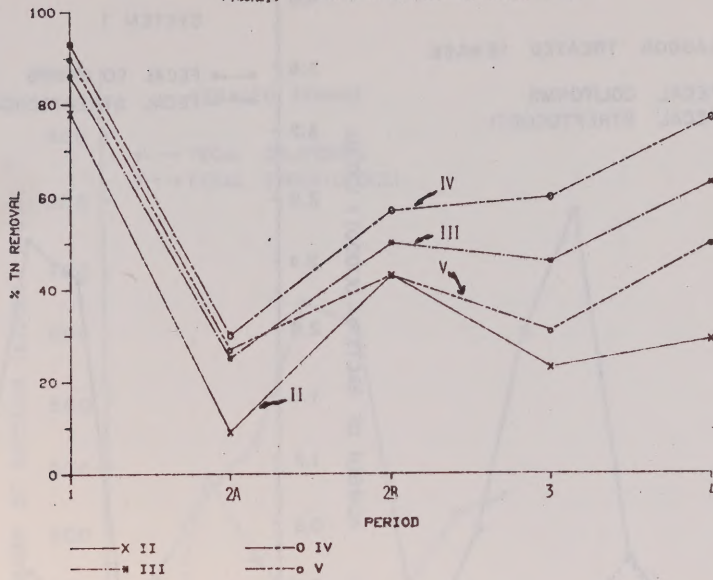
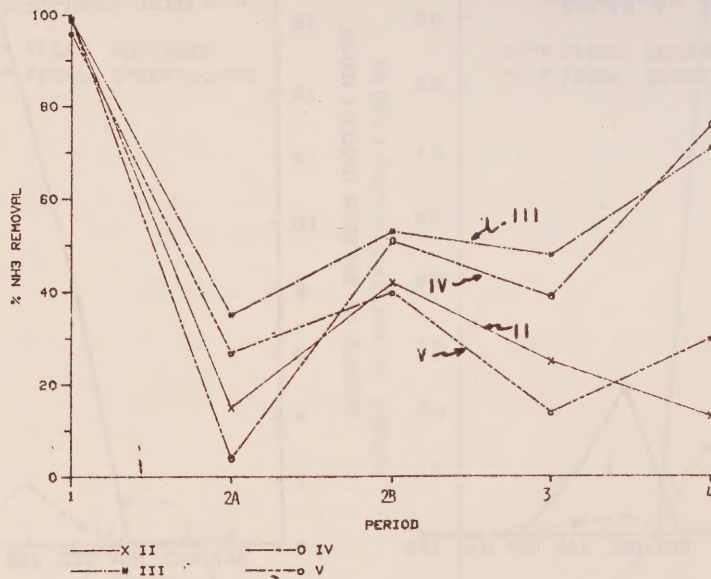


FIGURE 17 - PERCENT NH₃ REMOVALS FOR SYSTEMS II & V



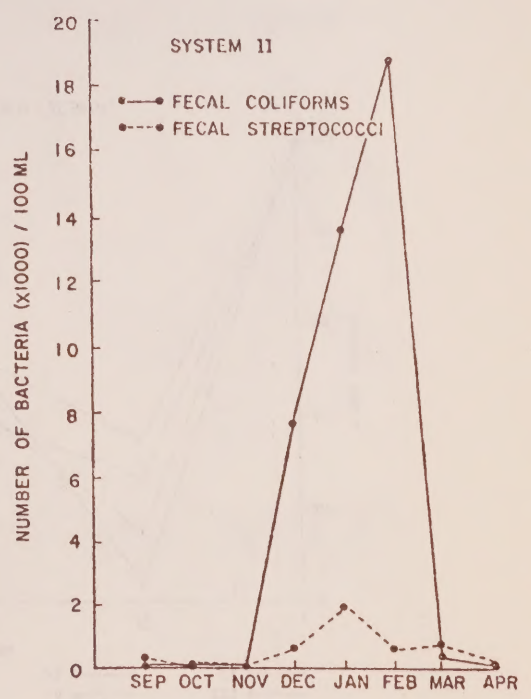
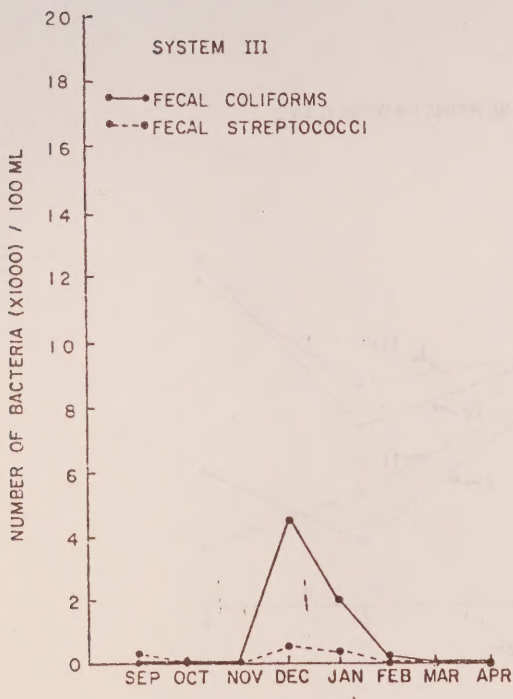
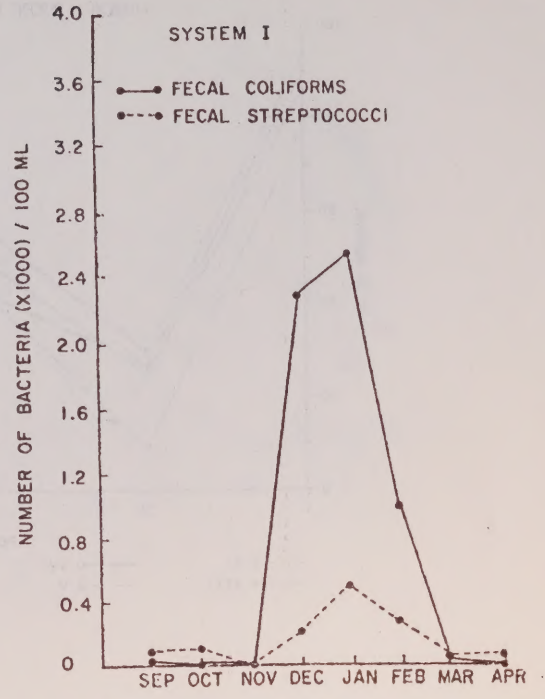
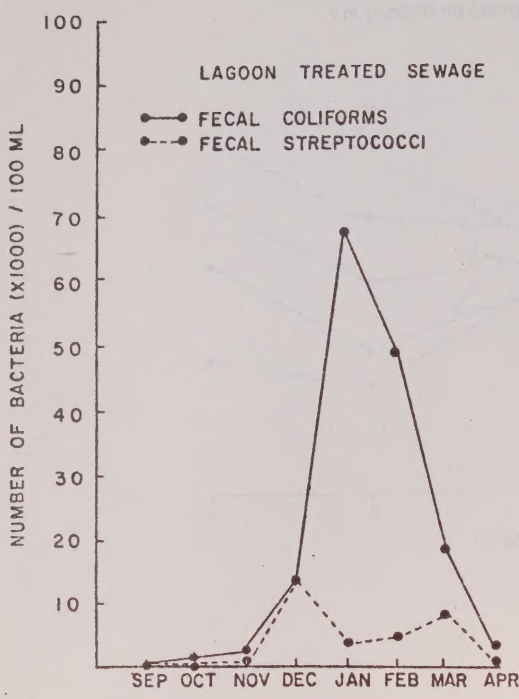


Figure 18: Bacterial populations in lagoon influent and systems I-III.

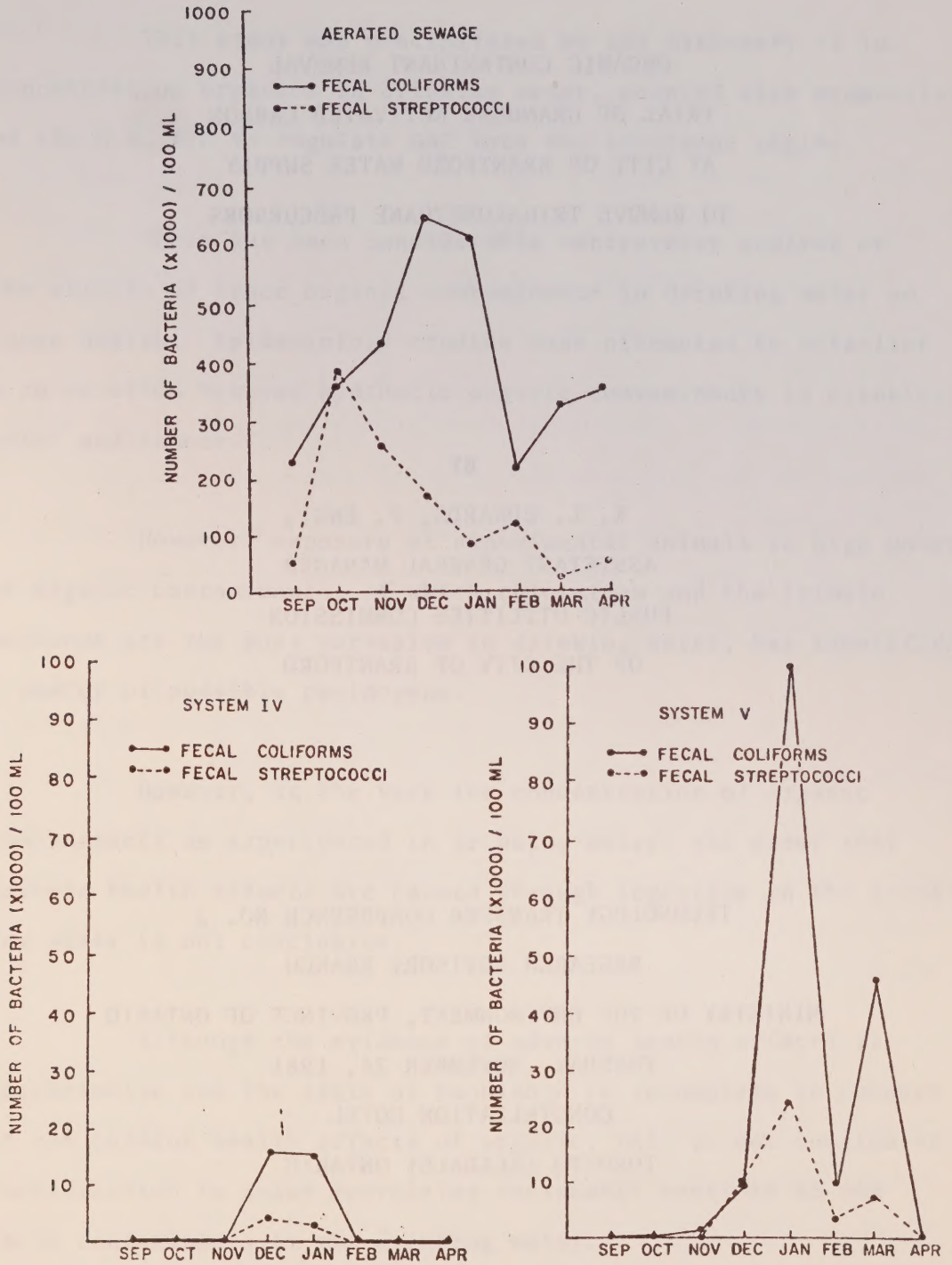


Figure 49: Bacterial populations in raw sewage influent and systems IV & V.

ORGANIC CONTAMINANT REMOVAL
TRIAL OF GRANULAR ACTIVATED CARBON
AT CITY OF BRANTFORD WATER SUPPLY
TO REMOVE TRIHALOMETHANE PRECURSORS

BY

K. L. EDWARDS, P. ENG.,
ASSISTANT GENERAL MANAGER
PUBLIC UTILITIES COMMISSION
OF THE CITY OF BRANTFORD

TECHNOLOGY TRANSFER CONFERENCE NO. 2
RESEARCH ADVISORY BRANCH
MINISTRY OF THE ENVIRONMENT, PROVINCE OF ONTARIO
TUESDAY, NOVEMBER 24, 1981
CONSTELLATION HOTEL
TORONTO (REXDALE) ONTARIO

This study was precipitated by the discovery of low concentration organics in drinking water, coupled with proposals of the U.S. EPA to regulate GAC into the treatment regime.

There has been considerable controversy centred on the effects of trace organic contaminants in drinking water on human health. Epidemiology studies have attempted to establish a correlation between synthetic organic contaminants in drinking water and cancer.

However, exposure of experimental animals to high doses of organic contaminants, of which chloroform and the trihalomethanes are the most pervasive in drinking water, has identified a number of possible carcinogens.

However, at the very low concentration of organic contaminants as experienced in drinking water, the proof that adverse health effects are caused through ingestion in the drinking water is not conclusive.

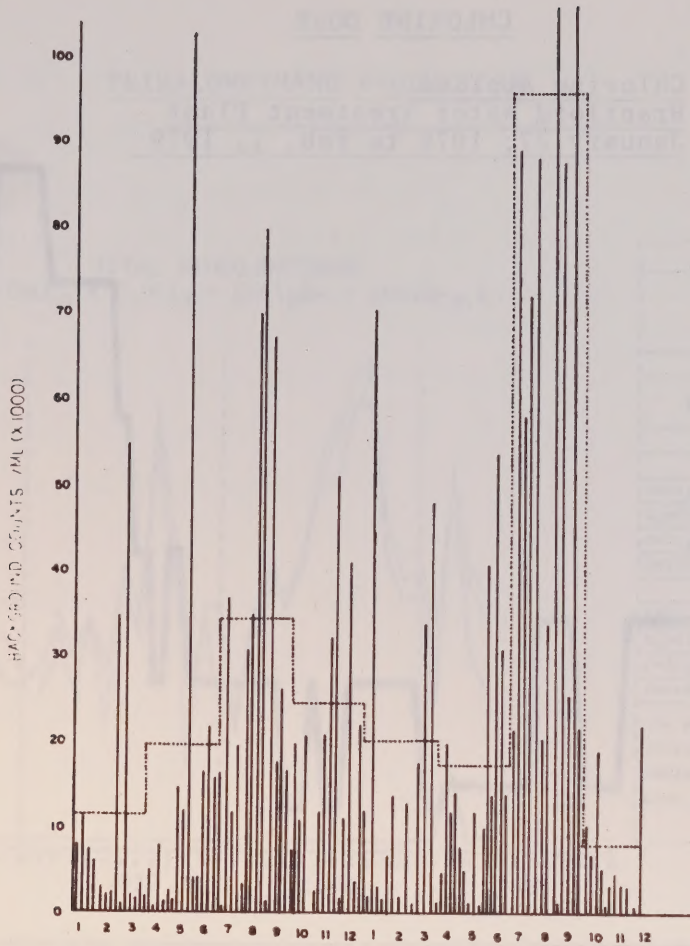
Although the evidence of adverse health effects is inconclusive and the state of knowledge is incomplete in respect of the harmful health effects of organic, this is not considered justification to delay exercising reasonable controls to minimize contaminants in the drinking water.

The identification of trace synthetic organics in the Grand River water shed and the occurrences of volatile organohalides formed by the chlorination disinfection process provided the impetus necessary to initiate a pilot plant study at the Brantford Water Treatment Plant. The effectiveness and feasibility of removing trihalomethane precursors through the use of granular activated carbon in place of the rapid sand filter beds was to be studied. This pilot plant project has been active on an intermittent basis over the past thirty months. The approach to the study was to treat the pilot plant as a black box or a series of black boxes so that in and out qualities of the water could be monitored in relationship to changes in the treatment variables.

The treatment regime at the Brantford Water Treatment Plant includes superprechlorination, followed by powdered activated carbon for taste and odour removal, followed by alum and silicate application for flocculation and settlement, lime application for Ph control, rapid sand filters, and finally, fluoridation.

The raw water quality is highly variable. The catchment basin of the Grand River includes heavily populated areas with intensive agricultural and industrial activity. Much reliance for quality control of raw water in the watershed is placed on the many sewage treatment plants in the upper reaches of the Grand, including Cambridge, Kitchener, Guelph and Paris.

BACKGROUND BACTERIA



1979

1980

BACKGROUND BACTERIA

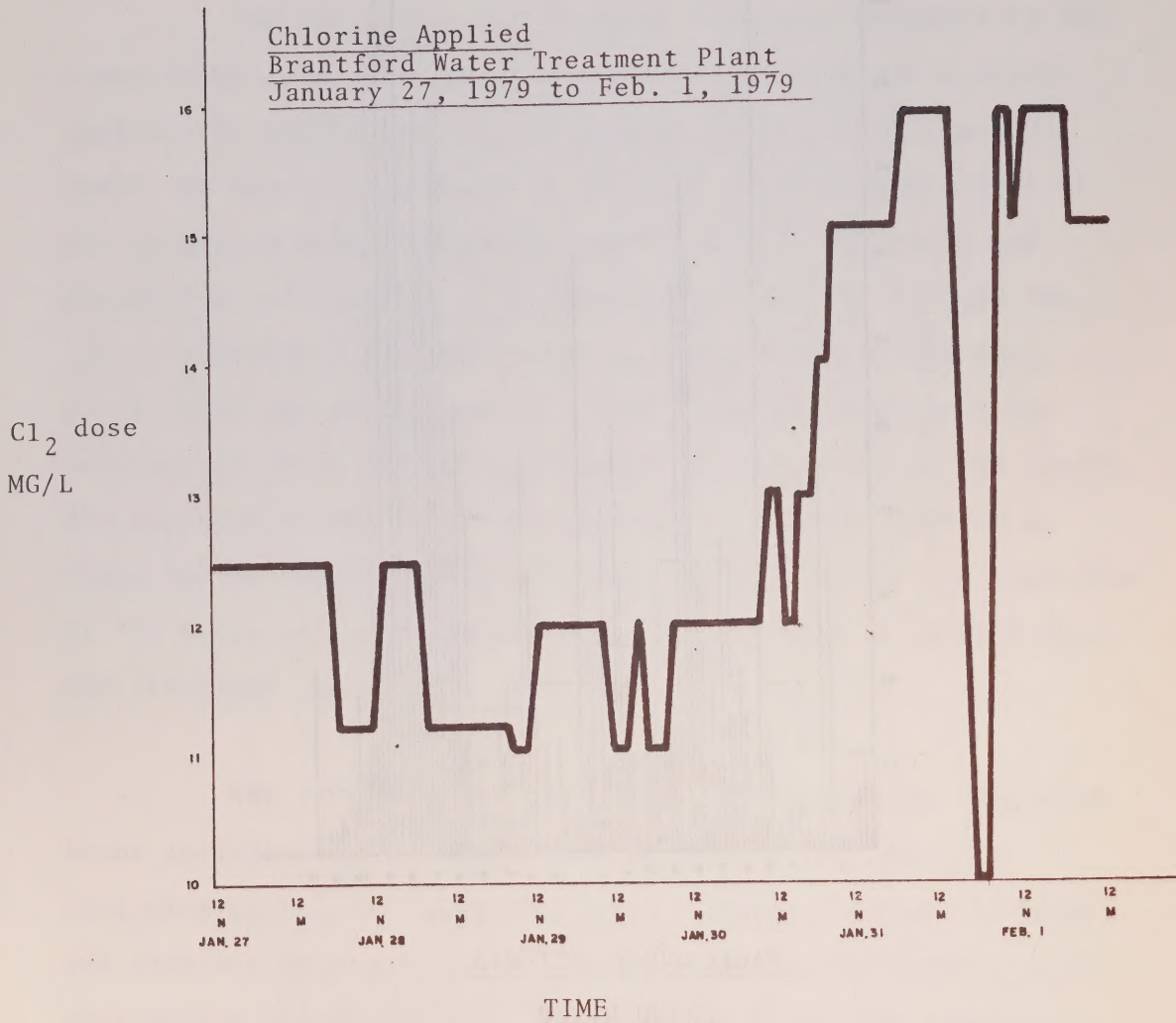
GRAND RIVER

AT BRANTFORD WATER TREATMENT PLANT

The background bacteria counts in the raw water are highly variable and unpredictable. A plot of the median value for each quarter generally has shown highest background counts are experienced in the third quarter and lowest counts are seen in the fourth quarter as evident in this graph for 1979 and 1980.

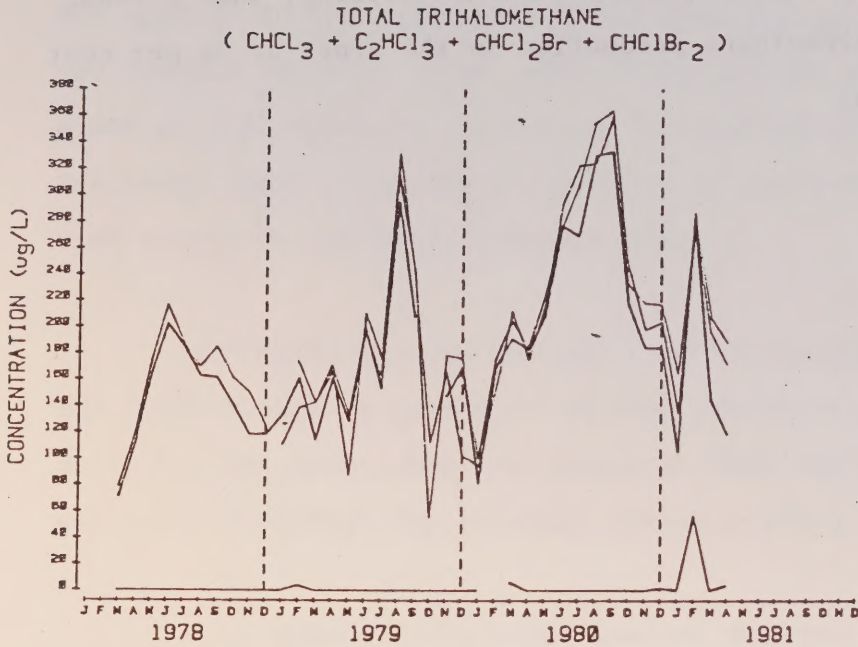
CHLORINE DOSE

Chlorine Applied
Brantford Water Treatment Plant
January 27, 1979 to Feb. 1, 1979



The chlorine demand of the raw water is also extremely variable. This graph of the chlorine dose applied to the raw water to produce a constant free residual, taken at random for a week in January, 1979, indicates fluctuations from 10 to 16 mg/l chlorine dose, occasionally in a matter of hours.

TRIHALOMETHANE PRODUCTION



LOCATION		
BRANTFORD		
REGION		
WEST CENTRAL		
% of TTHM		
	1978	1979
CHCl_3	85.8	87.5
C_2HCl_3	2.7	2.3
CHCl_2Br	12.6	11.8
CHClBr_2	8.8	2.4
	1980	1981
CHCl_3	87.7	85.6
C_2HCl_3	---	2.2
CHCl_2Br	12.3	13.3
CHClBr_2	---	2.6
RAW BLUE-UNDQUENCHED		
TREATED BLUE-UNDQUENCHED		
TREATED RED-QUENCHED		
DIST. BLUE-UNDQUENCHED		

The trihalomethanes analysed in the finished water vary throughout the year as shown in this graph of 1978 through 1981. Highest readings are again found in the third quarter when temperatures are up and plant growth is at its peak.

I would note that all THM analysis for this study used the Ministry of the Environment's D.A.I. methods which I'm told produces results approximately 1.9 times greater analysis via purge and trap methods.

Before beginning the pilot plant study, we were also advised that jar testing at the Ministry of the Environment labs had indicated that by removing prechlorination and delaying the chlorination until after flocculation and settling, that a reduction of the trihalomethane production in the order of 90 per cent might be achieved.

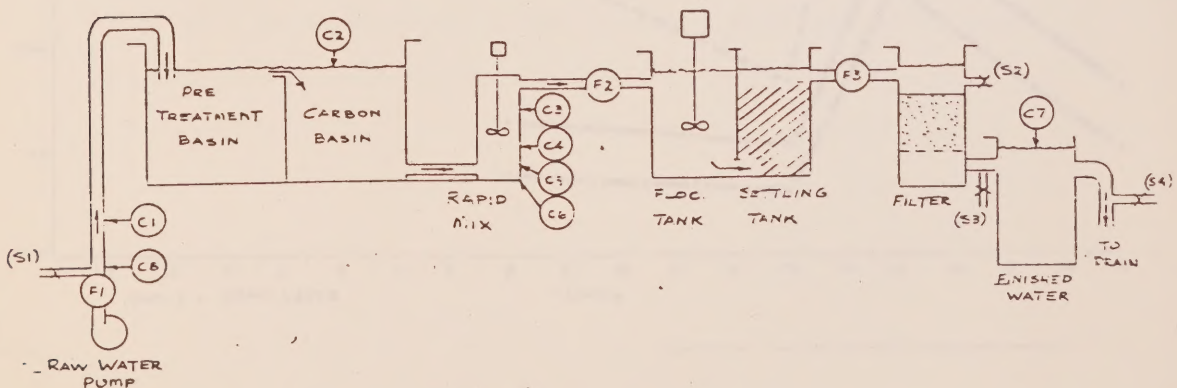


The pilot plant was set up in parallel with the Brantford Water Treatment Plant. Powdered activated carbon was not applied to the water except for examination of that material for organic removal. Lime application was not used in the pilot plant as only minor Ph correction is required at the Brantford Treatment Plant to maintain stability of calcium carbonate and iron pickup in the distribution system.

Prechlorination was not used in the pilot plant because the study wished to determine whether precursory removal was possible, not trihalomethane removal. Thus the raw water Ph was not reduced through the prechlorination process.

In general, the water quality was monitored in the raw state after settling and after filtering to determine the presence of bacteria, and precursors to the formation of trihalomethanes.

PILOT PLANT SCHEMATIC



CHEMICAL APPLICATION LOCATIONS

C1 - PRE CHLORINATION

C3 - ALUM

C5 - ANHYDROUS AMMONIA

C7 - POST CHLORINATION

C4 - ALKALINE

C6 - ALKALINE

C8 - POTASSIUM PERMANGANATE

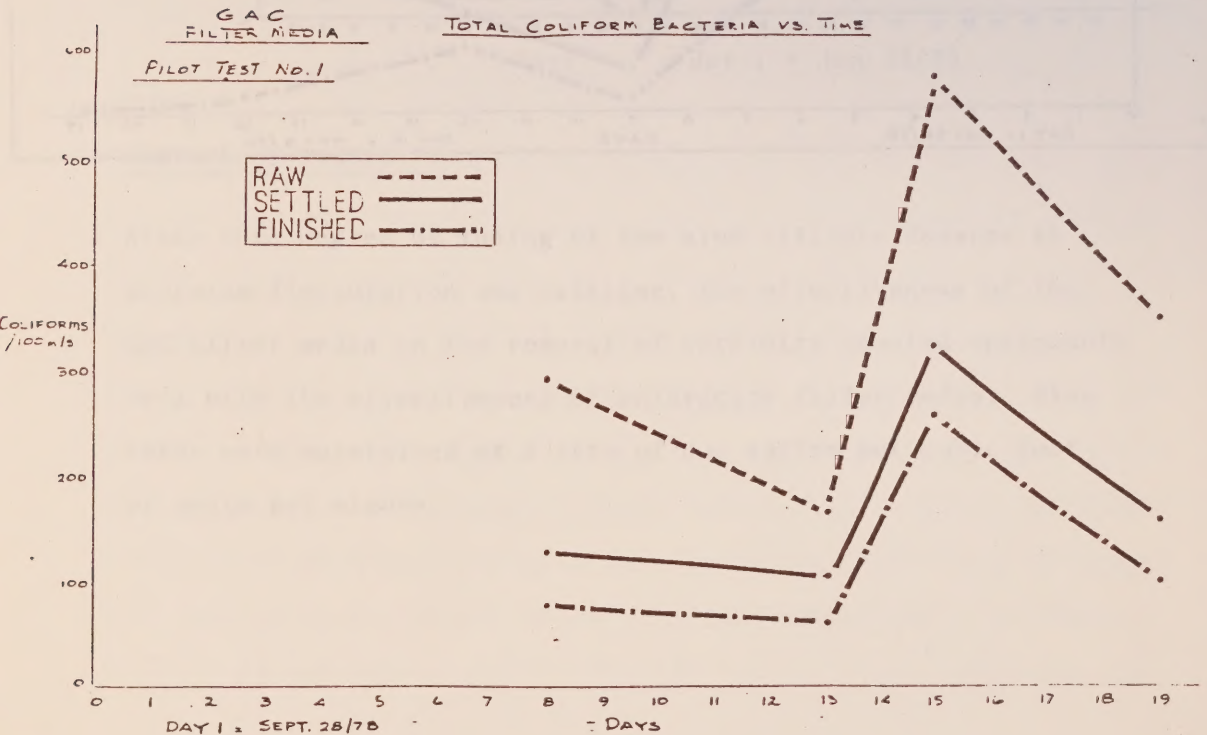
C9 - POTASSIUM PERMANGANATE

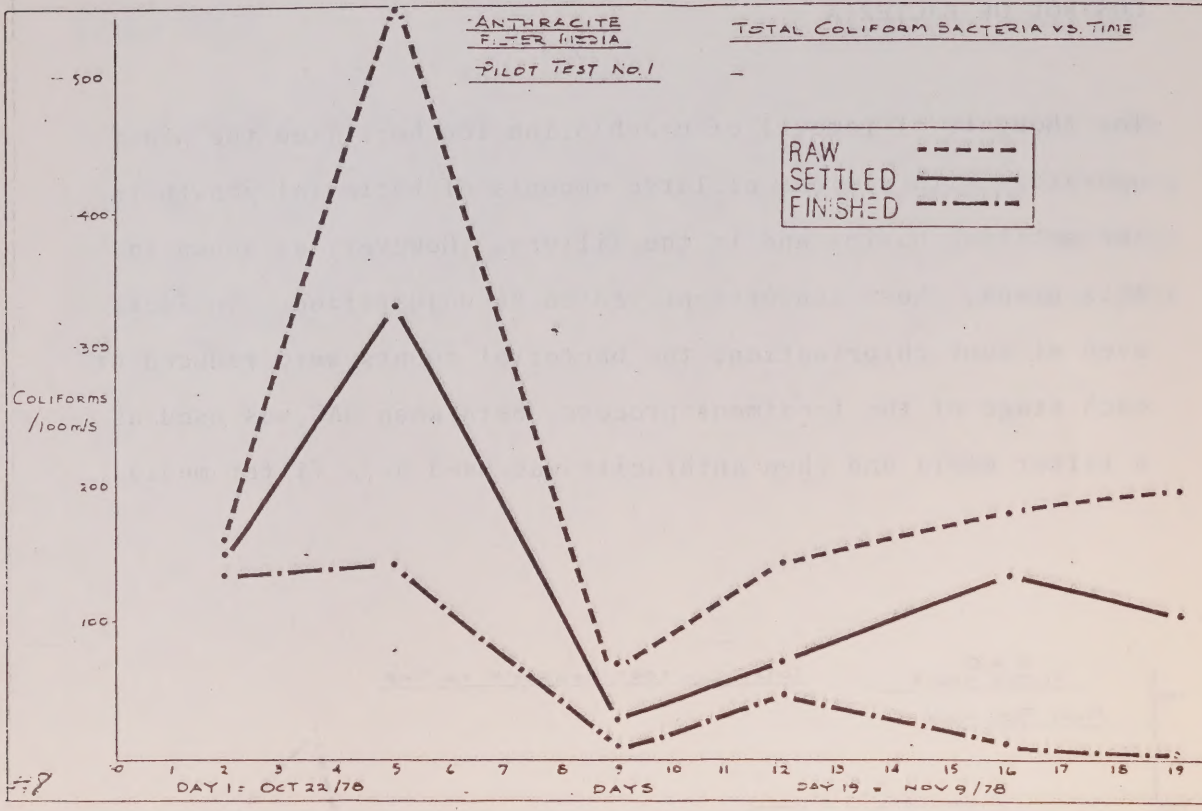
PILOT STUDY

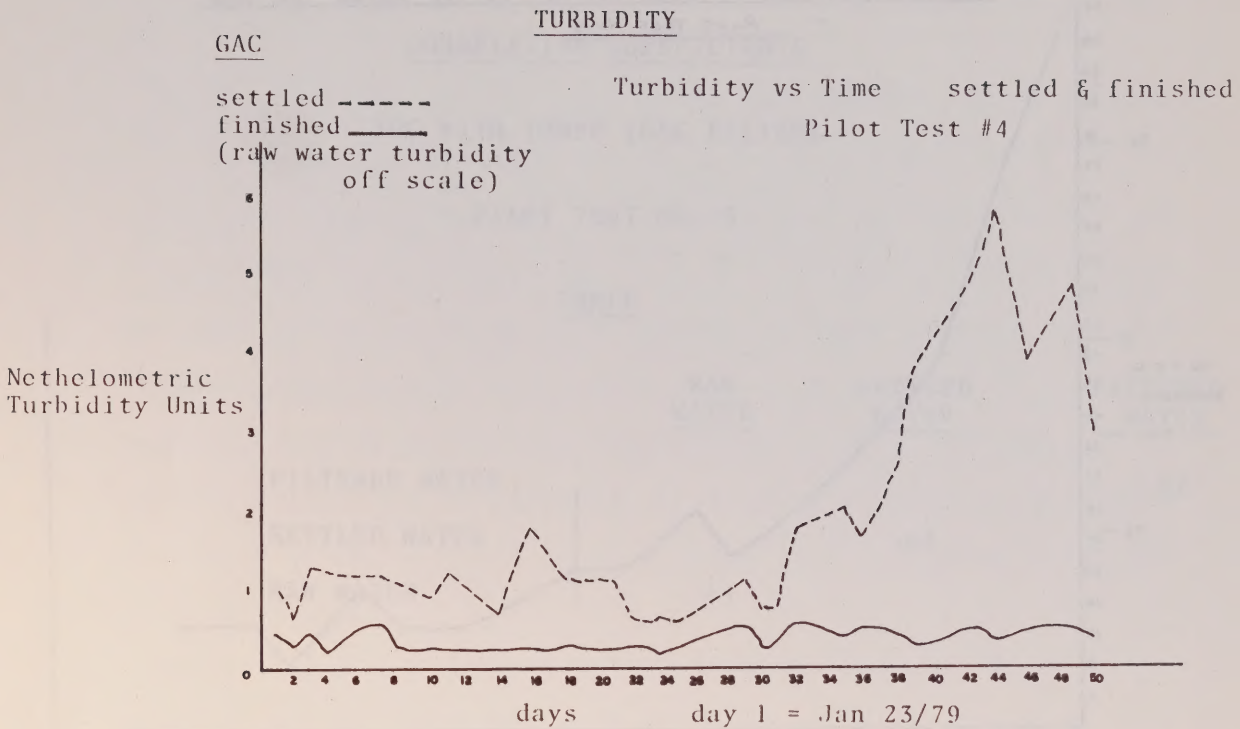
I will not attempt to cover all the avenues which this study took us down, many of which turned out to be deadends and many of which required repeating due to knowledge gained along the way, but will only highlight those points where reasonable conclusions were felt to be reached.

CONTROL OF BACTERIA

The thoughts of removal of prechlorination horrified the plant operators with visions of large amounts of bacterial growth in the settling basins and in the filters. However, as shown in this graph, these concerns proved to be unjustified. In fact, even without chlorination, the bacterial counts were reduced at each stage of the treatment process, both when GAC was used as a filter media and when anthracite was used as a filter media.

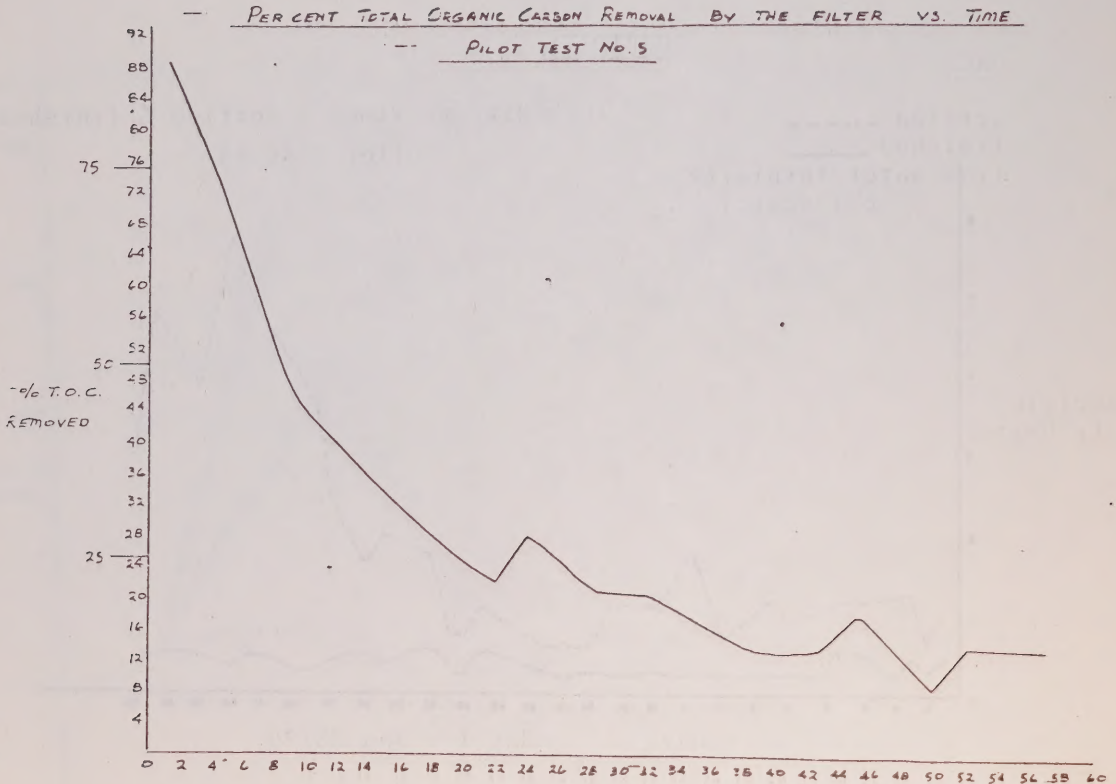






CONTROL OF TURBIDITY

After some degree of tuning of the alum silicate dosages to maximize flocculation and settling, the effectiveness of the GAC filter media in the removal of turbidity equated reasonably well with the effectiveness of anthracite filter media. Flow rates were maintained at a rate of one gallon per cubic foot of media per minute.



CONTROL OF TOC

We observed that in excess of seventy-five per cent of the TOC was removed by a new gas carbon filter. However, after a period of a few weeks, the percentage reduction of TOC was reduced to less than twenty-five per cent and continued to decline slowly from that point. The percent removal appeared to stabilize after about 30 days. In comparison results of TOC reduction through anthracite filter media were much lower - generally less than six per cent.

CORRELATION COEFFICIENTS

TOC WITH THMFP (GAC FILTER)

PILOT TEST NO. 5

THMFP

	<u>RAW WATER</u>	<u>SETTLED WATER</u>	<u>FILTERED WATER</u>
FILTERED WATER			.82
SETTLED WATER		.64	
RAW WATER	.45		

On the premise that TOC might be monitored to reflect THM, an attempt was made to establish a correlation between TOC and THMFP. Little success was had. However, it should be noted that the correlation of TOC with trihalomethane formation potential was considerably improved after the water had passed through the carbon filter. The inference of this observation is, of course, that the carbon filter may have been more effective in removal of organics which are not precursors to trihalomethanes. One would have to question further whether non-precursors consume the ability of the carbon to absorb organics.

CONTROL OF PRECURSORS

I would first comment that at no time were we able to achieve in the pilot plant reductions of the THMFP in the order of 89 - 90 per cent as indicated in jar test techniques, but that only a disappointing 10 - 30 per cent reduction of THMFP was achieved through delay of chlorination until after the settling basins. It is worth noting at this point that erratic results in the monitoring of trihalomethane production through chlorination caused us to retrace many of our steps after we were well into the pilot study.

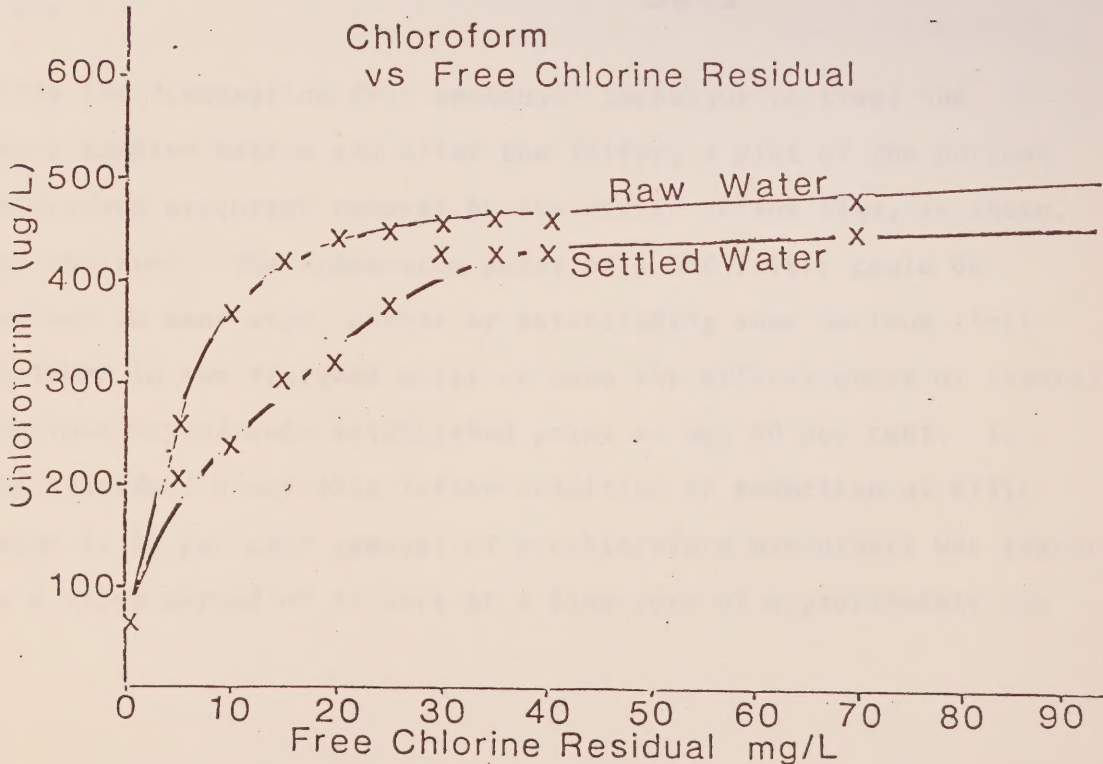
At the commencement of the study, it was determined that we should hold the chlorine dose constant for applications to all samples to monitor trihalomethane production. A level of 10 milligrams per litre was chosen as this was the average annual dosage in the Brantford Water Treatment Plant.

SELECTED CHLOROFORM OBSERVATIONS

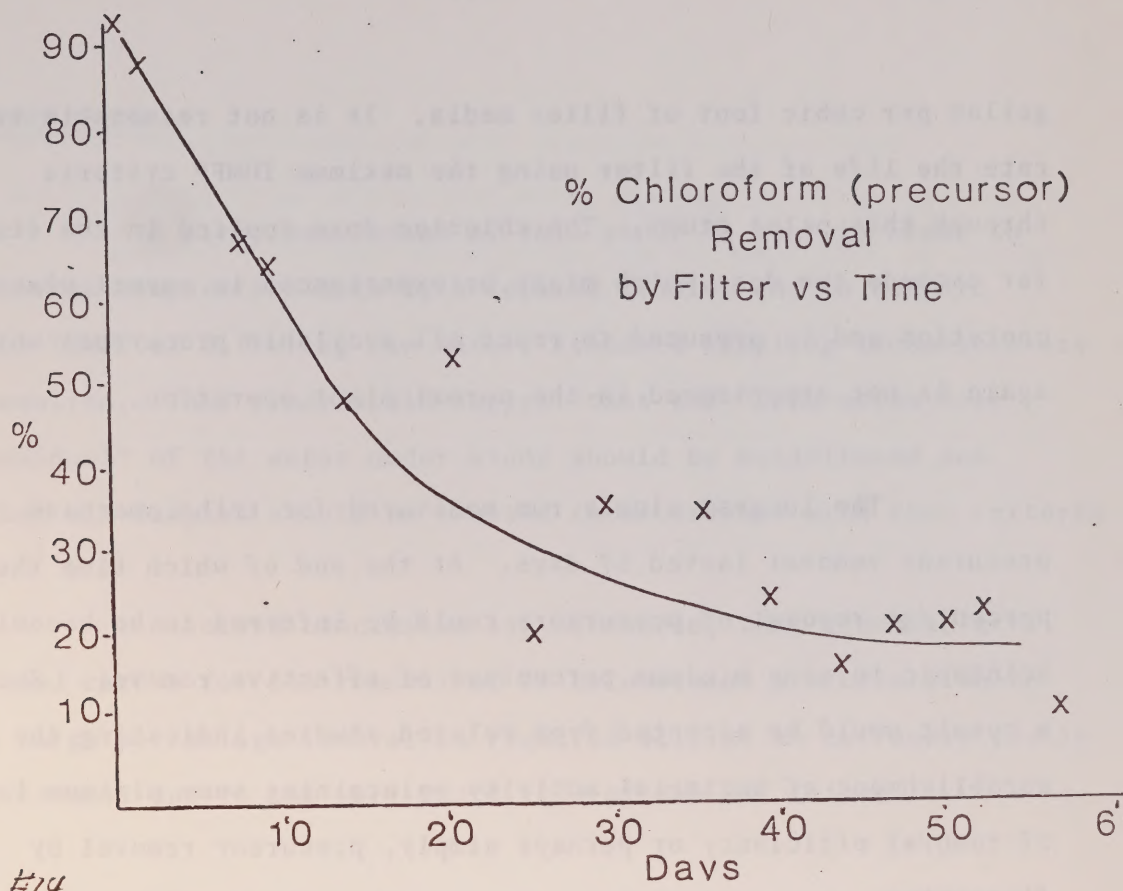
PILOT TEST NO. 4

Day	Production of CHCl_3 with 10 mg/l Chlorine Dose		
	<u>Raw Water</u>	<u>Settled Water</u>	<u>Finished Water</u>
7	70	79	79
21	23	16	14
31	10	10	8
43	58	33	30
49	60	65	70

It was noted that at times the trihalomethane results became very erratic and in fact on occasion trihalomethanes produced in the finished filtered water exceeded those produced when raw water was chlorinated. These observations lead us to the hypothesis that the trihalomethane formation potential was not directly related to the chlorine dosage but was in fact a function of the free chlorine residual. This hypothesis explained the higher trihalomethane production in the finished water. On occasion, the chlorine demand was reduced through the settling and filtering process, allowing a greater free residual chlorine to remain in the finished water to react with precursors to form trihalomethanes.



The hypothesis was tested in laboratory scale. The chloroform production appeared to be extremely dependent on the free chlorine residual particularly just above break point chlorination. This lead us to coin the term "saturation free chlorine residual" which was defined as a free chlorine residual above which one additional milligram per litre of chlorine added to the water would not produce more than one additional microgram per litre of chloroform. This required that many of the trihalomethane tests be repeated with samples chlorinated to provide a free residual above the defined saturation level which required application of in excess of 50 milligram per litre chlorine dose. This is, of course, far above what would normally be required in a full scale water treatment plant. However, this high chlorine dose was considered necessary to react all available precursors for the formation of trihalomethanes and to provide consistent results.



Using the "saturation free residual" technique to treat the water samples before and after the filter, a plot of the percent chloroform precursor removal by the filter versus time, as shown, was observed. The exhaustion point of a GAC filter could be defined in many ways, either by establishing some maximum limit of THMFP in the finished water or when the effectiveness of removal declines beyond some established point as say 50 per cent. In the Brantford study this latter condition of reduction of efficiency to 50 per cent removal of prechloroform precursors was reached in a short period of 15 days at a flow rate of approximately one

gallon per cubic foot of filter media. It is not reasonable to rate the life of the filter using the maximum THMFP criteria through this pilot study. The chlorine dose applied in the study far exceeds the dose which might be experienced in normal plant operation and is presumed to react all available precursors which again is not experienced in the normal plant operation.

The longest single run monitored for trihalomethane precursor removal lasted 57 days. At the end of which time the percentage removal of precursors could be inferred to be becoming acintopic to some minimum percentage of effective removal. Such a result would be expected from related studies indicating the establishment of bacterial activity maintaining some minimum level of removal efficiency or perhaps simply, precursor removal by filtration.

CONCLUSION

A first conclusion of this study is that in order to provide comparative data with related studies and to compare the THMFP of differing raw water, standard sampling techniques are required. This study would suggest that the "saturation free residual" of the water under study should be established and that all samples should be treated in accordance with that criteria.

A second conclusion is, of course, that granular activated carbon for the removal of trihalomethane precursors where a large percentage removal is required will be an extremely costly treatment due to the very short life of the GAC filter.

This study inferred some minimum percentage removal over a long period, which may have some application where a small percentage removal is desirable. However, longer term studies would be required to confirm the continued efficiency over the long run.

Finally, although not related to GAC, it was concluded that delaying chlorination until after flocculation and settling will reduce trihalomethane production. A practical assessment of such a change and evaluation of possible side effects of delaying prechlorination will be made at the Brantford Water Treatment Plant.

Some areas of analysis have not been concluded as tests of effectiveness of powered activated carbon for trihalomethane control so that some further results may yet be extracted.

ACKNOWLEDGEMENTS

I would like to express my appreciation for the assistance to this project from Hugh Ellis and the staff of the Brantford Water Treatment Plant, Ron Hunsinger and Ken Roberts of the Ministry of the Environment, Dan Oberski, my research assistant, Ron Gordon and Harry Dawson of Atlas Chemical, Roy Whitehead of Enviroclean and of course the "Provincial" lottery that funded the project through the Research Advisory Committee of the Ministry of the Environment.

THE EFFECT OF HYDRAULIC CHARACTERISTICS
AND EFFLUENT CHLORINATION ON THE
INCIDENCE OF MICRO-ORGANISMS OF PUBLIC
HEALTH SIGNIFICANCE IN RECEIVING WATERS

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TECHNOLOGY TRANSFER CONFERENCE 2

24 November 1981

ABSTRACT

Beak Consultants Limited (BEAK) were retained by the Ontario Ministry of the Environment (MOE) in the spring of 1979 to investigate the Effect of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-organisms of Public Health Significance in Receiving Waters, a project sponsored by the Ontario Lottery Fund.

A study program was designed to collect data on any possible parameter(s) which may influence the presence and kinetics of these micro-organisms in surface receiving waters. Consequently, this program involved primarily the compilation of an extensive and intensive data base. The analysis of this data and development of conclusions and specific recommendations was undertaken as a secondary objective.

The first phase of the study involved two MOE-operated sewage treatment plants during 1979-1980 at Grand Valley on the Grand River and at Ingersoll on the Thames River. The second phase of the operation (1980-1981) involved studies of the municipally operated sewage treatment plants at Peterborough on the Otonabee River and Port Hope on the north shore of Lake Ontario. Effects of chlorinated and non-chlorinated effluents on bacterial populations in the receiving waters were assessed.

For each site selected, hydraulic, micro-biological and chemical tasks were delineated. These tasks involved: time of travel, plume characterization and mixing zone determinations; meteorological data collection; routine and intensive sampling; field bacterial analysis of water and sediment; water quality characterization and quality assurance programs.

Data obtained from the studies showed that, in most cases, significant bacterial activity was evident and relationships were developed to provide a meaningful intercomparison. Correlations were made between indicator bacteria and pathogens as well as amongst the indicators themselves. Bacterial kinetics were evaluated where data indicated significant decay activity was taking place.

INTRODUCTION

Chlorine disinfection of water has been a standard and widespread practice since it was first introduced at the start of this century. This practice, once accepted, has thrived over the years as it has proven remarkably effective in controlling waterborne bacterial diseases. Recently, the chlorine disinfection process has come under increased scrutiny as environmental side effects of chlorinated compounds come to the attention of the scientific community.

The process of chlorination of sewage plant effluents has been widely adopted for the destruction of residual pathogenic micro-organisms. The two most common forms of treatment involve the continuous addition of either hypochlorite (sodium or calcium) or chlorine gas to the effluent, resulting in the formation of chloramines. The chlorine disinfection process results in the conversion of the higher oxidation state chlorines to chloride. Disinfection of domestic waste treatment effluent is often considered adequate when a combined available residual of 0.5 mg L^{-1} is achieved after 15 minutes of contact.

The International Joint Commission has recently proposed a residual chlorine water quality objective which would require many Ontario treatment plants to dechlorinate effluents or employ alternative forms of disinfection. At considerable cost, effluents could be rendered non-toxic to aquatic life by eliminating chlorine residuals; however, chlorinated organic compounds or, alternatively, ozonated compounds could still pose an environmental health problem. Clearly, the preferred solution would be to not disinfect at all, or at certain times, if the die-off of pathogenic bacteria could be left to natural conditions with assurance that public health would not be jeopardized.

In June 1979, the Ontario Ministry of the Environment (MOE) selected Beak Consultants Limited (BEAK) to carry out a study supported by the Provincial Lottery Fund to investigate hydraulic, water quality, and atmospheric conditions which contribute to the die-off of bacteria from chlorinated and non-chlorinated sewage effluents in receiving waters.

The Ontario Ministry of the Environment established a Liaison Committee comprising Ms. A. Vajdic, Dr. H. Gowda, and Dr. D. Rokosh to participate in the study in an advisory capacity and to assist in the determination of study sites, methodology and program design.

STUDY OBJECTIVES

In order to successfully assess the advantages and disadvantages of sewage chlorination, it was necessary to address several factors. The objectives of the study were:

1. to determine the incidence of pathogenic bacteria and indicator bacteria in sewage treatment plant effluents and their receiving waters, both with sewage chlorination and without;
2. to determine if, in these waters, chlorination results in a significantly lower concentration of pathogenic bacteria than in the case of non-chlorinated effluents;
3. to investigate those hydraulic, water quality, and atmospheric conditions which contribute to the natural die-off of pathogenic bacteria in non-chlorinated effluents and their receiving waters. The results should logically lead to the development of guidelines and criteria for effluent disinfection in Ontario;
4. to determine the need and desirability to use selected pathogenic bacteria in place of indicator organisms as a measure of conditions hazardous to public health in effluents and receiving waters in Ontario, particularly where and when effluents are not chlorinated.

A study plan was set up based on a three-phase, three-year approach. Year 1 involved two plants discharging to riverine environments; year 2 included one plant with riverine and one plant with lacustrine receiving waters; year 3 comprised co-ordination studies, data interpretation, and final report submission.

The program was designed to encompass these concerns and this timetable addressed itself to several critical elements in the investigation.

Analytical accuracy and consistency were essential to the execution of this study. In order to achieve the highest possible analytical standards and to establish confidence in these findings, several measures were incorporated in the scope of work.

Bacteriological analyses were conducted on-site in a mobile field laboratory. This permitted analyses to commence within one to four hours of the time of sample collection, regardless of sampling location.

Methodology was carefully reviewed with the Liaison Committee before the program was initiated, as well as throughout the field period. Investigation of media suitability, recovery and confirmation of colonies was carried out routinely to establish quality control.

Rigorous quality assurance studies were carried out with the MOE Taxonomy Section participating as the external reference laboratory.

The study approach was to measure as many factors as possible that influence bacterial growth and mortality, simultaneously with the bacterial monitoring of receiving waters. The factors considered were:

1. hydraulic characteristics of the receiving water, including time of travel, velocities, and cross-sectional profiling;
2. water quality characteristics including any waterborne chemical parameters which might be involved in interactions with biological organisms that could influence the propagation or die-off of these bacterial organisms;
3. characteristics of the in-stream sediments which could affect bacterial regrowth including sediment bacteria, macro-organisms and sediment classification;
4. meteorological factors influencing growth and die-off which include solar radiation, temperature, and precipitation. The lake study was also greatly affected by wind speed and direction.

SITE SELECTION

At the beginning of each study year a selection of treatment plants was made, based on the requirements of the study, availability of plant and ability to undergo periods of non-chlorination without endangering public health. In meetings between BEAK project personnel and the MOE Liaison Committee, Grand Valley on the Grand River and Ingersoll on the Thames River were selected for investigation during the first year. In the second year, Peterborough on the Otonabee River and Port Hope on Lake Ontario were chosen for study.

RIVER BASED STUDIES

GRAND VALLEY

MOE operates an extended aeration treatment plant for the town of Grand Valley. The facility is situated at the south end of the town and discharges to the Grand River via a sewer and a single outfall located on the west bank of the river. The effluent and receiving water are soon mixed, passing over a series of short pools and riffles for the first 0.5 km. There are no major tributaries or effluent sources between Grand Valley STP and Belwood. Station locations on the Grand River were determined based on the approximate time of travel at that time of year. Stations for chlorination and non-chlorination for each survey were the same. A map of the study area is presented in Figure 1.

INGERSOLL

Sewage from the town of Ingersoll is treated in a conventional secondary treatment facility operated by the Ontario Ministry of the Environment. The final treated effluent leaves the chlorination contact chambers and is discharged at the north shore of the Thames River downstream of Ingersoll via two outfalls, one from the new plant and one from the old plant, both open culverts with an armoured skirt to prevent erosion. The sampling periods were carried out at Ingersoll during September and December 1979, and February 1980. The stations extended westward from Ingersoll approximately 6 km and 12-18 hours time of travel. The Ingersoll study area is shown in Figure 2.

PETERBOROUGH

The Peterborough water pollution control plant is located on the east bank of the Otonabee River in the City's east side approximately 1.6 km downstream of Lock 19 of the Trent Canal System (Figure 3).

The facility is composed of two conventional secondary plants, one old and one new, which operate in parallel before discharging to a shared chlorine contact chamber operated on a liquid chlorine supply. Sewage effluent is chlorinated only between 15 May and 31 October.

The Peterborough STP treats an average 12 MIGD of sewage before discharge to the Otonabee River (1976 data). Sampling was undertaken during June and October 1980 on the Otonabee River and was carried out between the plant and Squirrel Creek, covering a zone of up to 10-16 hours time of travel.

STUDY OUTLINE

Eight stations were established for the river-based plants: a control above the outfall, the outfall stream and six downstream of the outfall, spanning a period of up to 12-18 hours time of travel after release to the receiving waters.

Surveys were carried out during separate seasons, based on a three-consecutive-day sampling during routine chlorination, followed by a 7-10 day stabilization period during which no chlorination was carried out at the plant. This stabilization period was followed by a second three-day sampling period at the termination of which, chlorination was recommenced.

Each three-day sampling period was comprised of a regular daily sampling at each station. Extra samples were taken on the first day of each three-day period to assess diurnal fluctuations in the background, effluent and mixing zone.

At Peterborough, cross-sectional sampling was carried out to assess lateral variation of bacterial and chemical concentrations.

Detailed chemical and micro-biological analysis was carried out for the following parameters:

Bacterial Parameters

Total coliform	(TC)
Fecal coliform	(FC)
Fecal streptococcus	(FS)
<u>Pseudomonas aeruginosa</u>	(PS)
<u>Klebsiella species</u>	(KB)

Chemical Parameters

Temperature	Nitrite
Dissolved oxygen	Ammonia
pH	Total Kjeldahl
Chlorine	nitrogen
Conductivity	Total Phosphate
Turbidity	Suspended solids
Nitrate	BOD (nitrification inhibited)

In order to relate these to physical (hydraulic) parameters, streamflow data was obtained from the Water Survey of Canada in Guelph and used in conjunction with time of travel determinations, made by monitoring the passage of a conservative tracer substance down the river. Meteorological parameters were measured by a six parameter met. station installed on site at the STP under investigation.

In addition, the mixing zone of the effluent was determined using a continuous low-level tracer injection and monitoring, as well as the cross-sectional area and cross-sectional velocities. This data was used to evaluate the extent of mixing in the effluent plume and to obtain a comparable concentration with other stations downstream of the mixing point.

LAKE BASED STUDIES

PORT HOPE

The Port Hope STP is located at the east end of Lake Street on the eastern edge of the town of Port Hope between Lake Ontario and the main railway lines. The effluent from both the old and new plants is chlorinated in a single 41 100 IG contact chamber operated on chlorine gas and having a retention time of 29.6 minutes at 2 MIGD load (1976). The effluent from the contact chamber is gravity-fed through a 60 cm diameter 350 m long outfall sewer (capacity 5.75 MIGD) to a T-shaped diffuser approximately 250 m out in Lake Ontario, 2-2.5 m beneath the surface. The nearshore area of Lake Ontario is shown in Figure 4.

STUDY OUTLINE

8 Stations were established within the plume. The stations were arranged to provide cross-plume samples and encompassed up to 8 hours total time of travel from the chlorine contact chamber. Surveys were carried out during July and September 1980 based on the same sampling schedule as outlined for rivers. Regular and intensive sampling was carried out concurrently with plume tracing. A conservative dye tracer was used to monitor the progress of the plume from release at the diffuser.

The intensity of sampling and analysis was identical to that previously outlined for the river-based plants. All parameters for water and sediment were the same; the hydraulic study was necessarily modified to allow evaluation of the unbounded discharge conditions present at Port Hope which result in a three dimensional multi-directional plume that has a variable mixing zone.

RESULTS

The bulk of data obtained for the sewage treatment plants studied was condensed to two volumes containing some 80-100 summary figures, maps and graphs and 100-120 summary tables of chemical, micro-biological and hydraulic data.

Data from Port Hope revealed very low input from the plant due to significantly lower loading than expected. This, combined with high background readings from the surrounding area implied that a far more detailed analysis would be required to evaluate the data base.

Since the study was designed as primarily a collection of data with only preliminary analysis, efforts were concentrated on the river based studies at this time.

For all three river-based sites an extensive data base was collected for chemical, bacteriological, hydraulic and meteorological analyses. In order to assess the extent of microbiological activity, the analytical results were corrected where possible to provide comparable data among stations. These corrections included cross-sectional averaging in the mixing zone based on sampling location, measured depth and velocity distributions to account for lateral variations and backtracked to determine the release time from the outfall. At release times, corresponding to each downstream station, measured flows and concentrations for both river and effluent were used to calculate the average mixed conservative in-stream concentration. This data was compared to the measured downstream data at the observed times of travel to provide an estimate of individual decay for each station for each bacteria type. For each river survey results from the bacteriological analysis were combined with the appropriate measured hydraulic data to provide a record of bacterial mass flow versus river time of travel.

This analysis, which explicitly considers the temporal behaviour of river flow and effluent discharge as well as the variation in both background and effluent bacterial concentrations, indicates a consistent trend in the data. At Grand Valley on the Grand River the mass of bacteria added to the river with and without chlorination is a very small fraction of the bacterial mass present due to background conditions. As a result any dynamic effects which may occur are masked by the natural variation in the data. For the data analyzed, with or without chlorination, the measured downstream bacterial mass is consistently at or below background levels.

For both Ingersoll on the Thames River and Peterborough on the Otonabee River, the additional mass added to the river during chlorination as a consequence of the effluent discharge is a larger percent of the endogenous or background bacterial mass. During periods of non-chlorination the effluent discharge contributes significantly to the background mass such that the mean mass flow in the river below the outfall is raised, in some cases, by approximately an order of magnitude. Apparent decay in bacterial mass to background levels downstream of the outfall is observed to occur at rates ranging from very rapid to very slow or not at all. This high degree of variation may be due to the lack of statistical certainty in the measured downstream bacterial data or it may be due to site-specific characteristics. Further analysis is required before any conclusions can be drawn.

In an attempt to carry out a limited assessment of bacterial kinetics, the data sets corrected to give the best estimate of concentration were converted to mass flow figures in counts per second. For each three-day sub-survey geometric means and deviations were calculated for the effluent and background values from all recorded measurements. These means and standard deviations of the generated conservative concentrations were plotted as a range from $\bar{C}_{ij} + S$ to $\bar{C}_{ij} - S$ as mass flow both for background and for background plus effluent. Figure 5 shows a typical plot for non-chlorinated conditions; squares linked by lines represent limits of background plus effluent and triangles represent best estimates of actual concentrations. Figure 6 shows a typical chlorinated condition, note that the limits for background and background plus effluent are coincident and measured values lie within the bounds as expected. Figure 7 shows a non-chlorination situation where hydraulic effects are present and shows how non-steady state dynamics further complicate the analysis.

Figure 8 shows an ideal case where effluent plus background is well above background and measured mass flow starts initially in the higher zone and decays back to within background limits.

Comparisons were made between each pathogenic organism measured and each indicator organism for all of the samples obtained during the study periods. These data set comparisons are presented as log-log plots in Figures 9 through 14 in order to determine if any relationship exists between pathogens and the traditionally measured indicator bacteria. Values of r noted on each plot indicate the correlation coefficient for that plot. Some of these plots show definite trends and it is likely that further investigation would be profitable although it has not been carried further in this project.

For each station sample, salmonellae were analyzed for on a present or absent basis on one day of each three-day survey. At Peterborough two positives were recorded in the effluent and outfall area during the second non-chlorination study. At Port Hope five positives were identified: one in the plant effluent during chlorination and four in the influent, effluent and receiving waters during non-chlorination. Four positive results were detected in the Grand River during the chlorination-on period; all in the receiving water downstream of the outfall. Ten positives were found at Ingersoll, one in the receiving waters during chlorine-on and the remainder from effluent and downstream stations during periods of effluent non-chlorination.

DISCUSSION

Analysis of bacterial data is usually made by comparing absolute numbers (colonies per 100 ml). The examination of the vast data base, obtained during this study, has attempted to present the data in some logically comparable form, correcting for changes in flow, cross-sectional variation, changes in plant operations and river conditions. Through the use of these modifications the data base has been reduced to a point where actual decay or regrowth may be seen. Normal comparisons lead to artificial decay or regrowth created by dispersion, dilution or changes in released effluent rather than being true decay or true regrowth. The methods of tracing residence time and backtracking to the time of release and determining "release conditions" show that not only can the effluent be effectively followed downstream, but that samples within a set can be accurately compared in a temporal framework where the actual effect of the river's actions is taken into account.

In addition comparable data is available for pathogenic bacteria: Klebsiella and Pseudomonas, as well as Salmonella (in an absent or present sense). Although the indicator organisms are easier to work with in a statistical sense, evaluations may also be made on the pathogens. The present study has taken the analysis of pathogenic bacteria to the stage of comparisons between each pathogen and each indicator organism as well as preliminary residence time versus pathogenic bacterial mass plots. A more in-depth analysis is required to develop decay rates and although the exercise looks fruitful, it is outside of the scope of the present study.

It must be restressed here that this project was essentially an extensive data collection study; analysis and investigation of the results was a minor component. The enormous data base obtained was examined in a very concise manner and general trends and relationships are apparent; however, the scope of the project has been met. Further, more detailed analysis looks promising in several areas and much of the non-bacterial data base has yet to be used. The nature of bacterial analysis and its inherent statistical scatter, compounded by non-steady state conditions of rivers, plants, inputs and climatology will necessitate a far greater and more detailed analysis than was possible here.

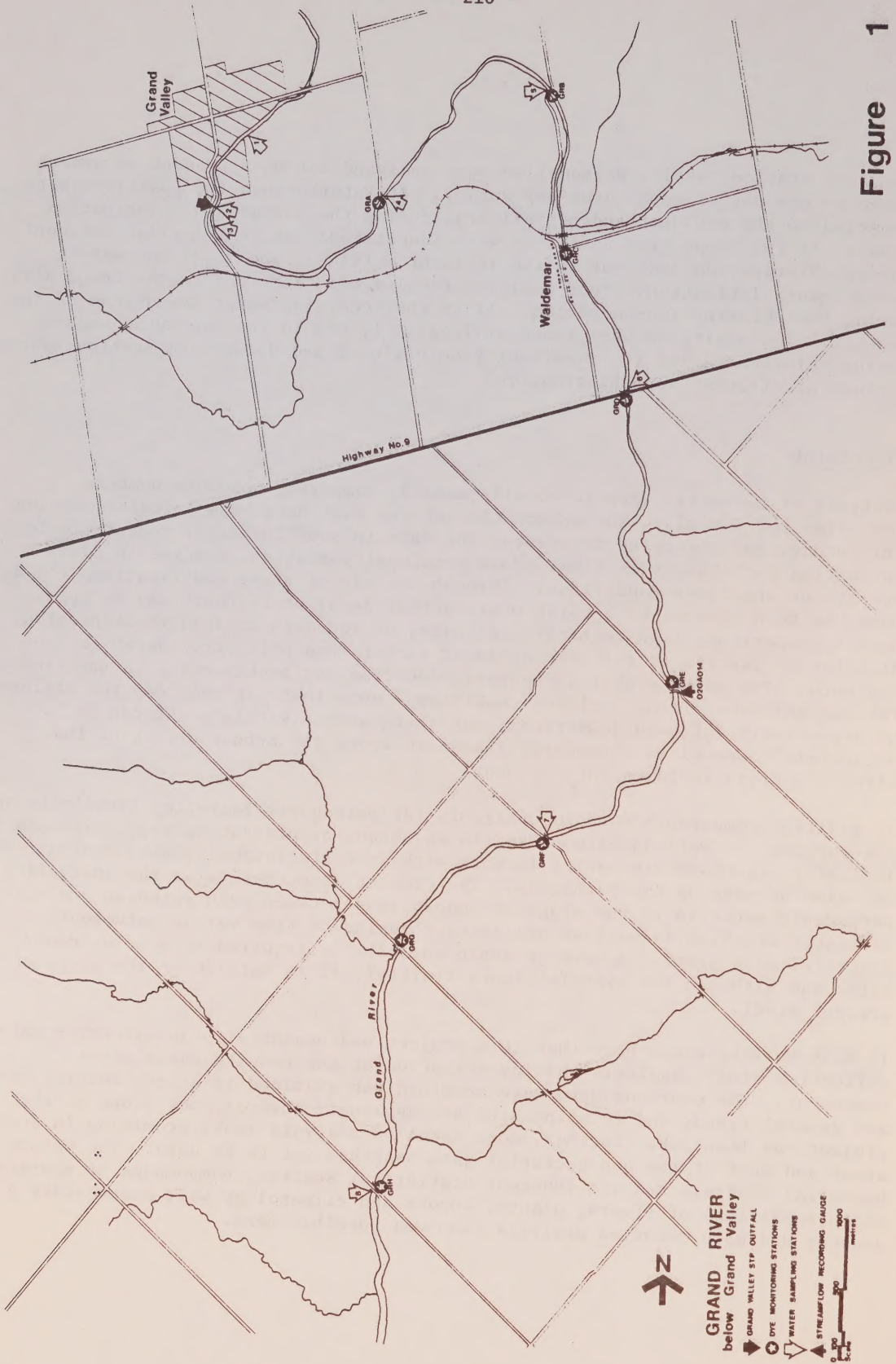


Figure 1

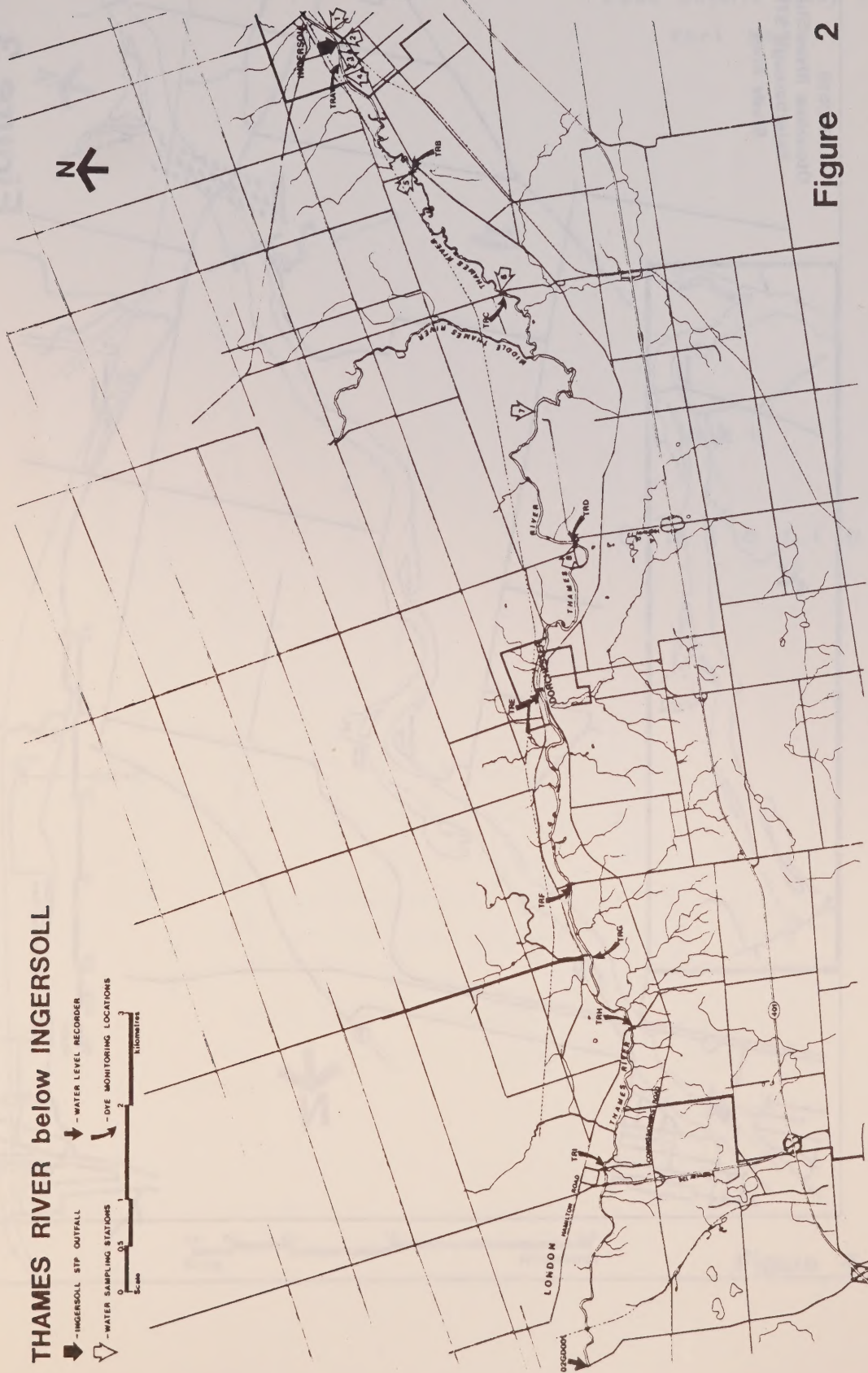


Figure 2

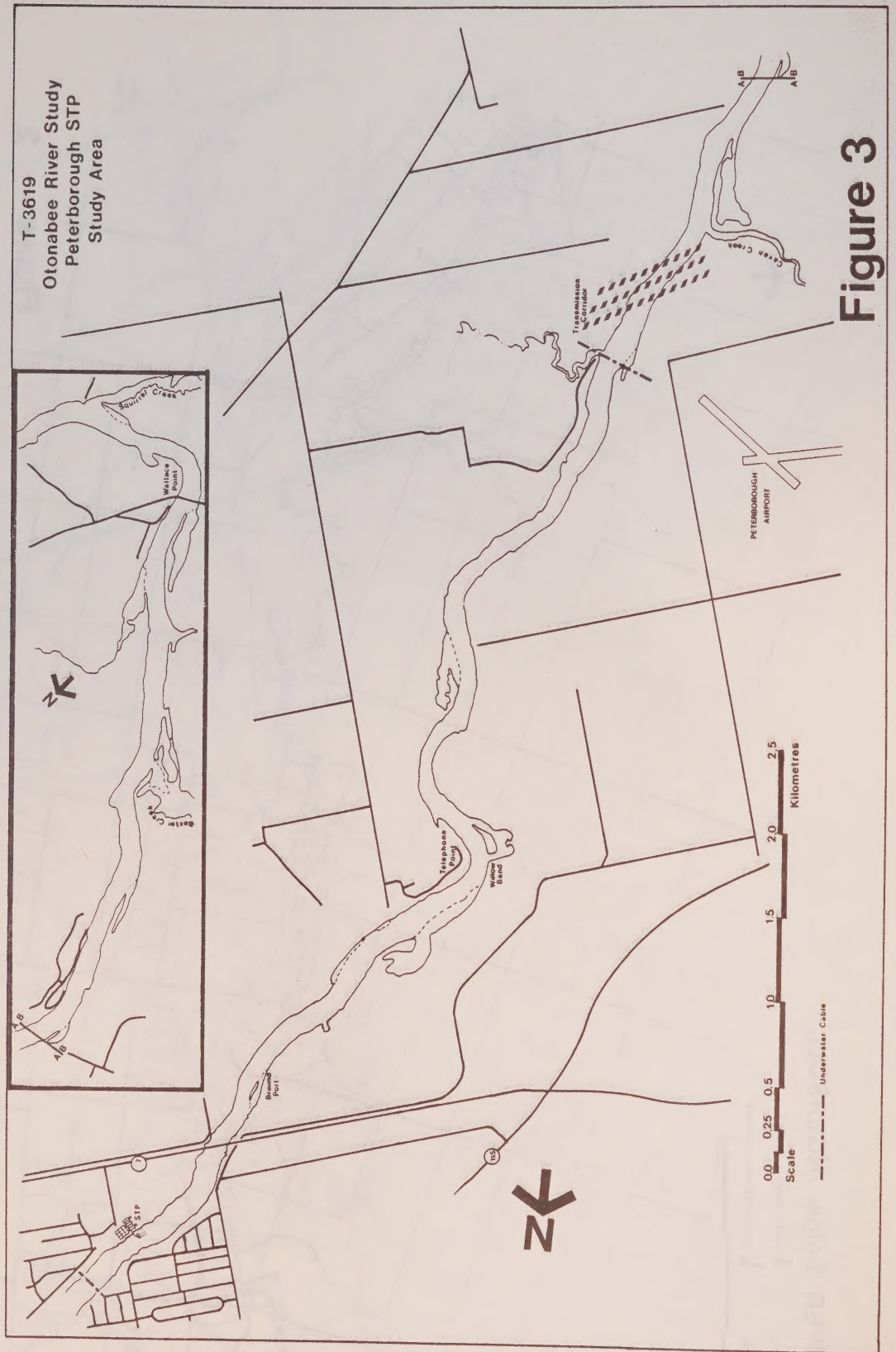
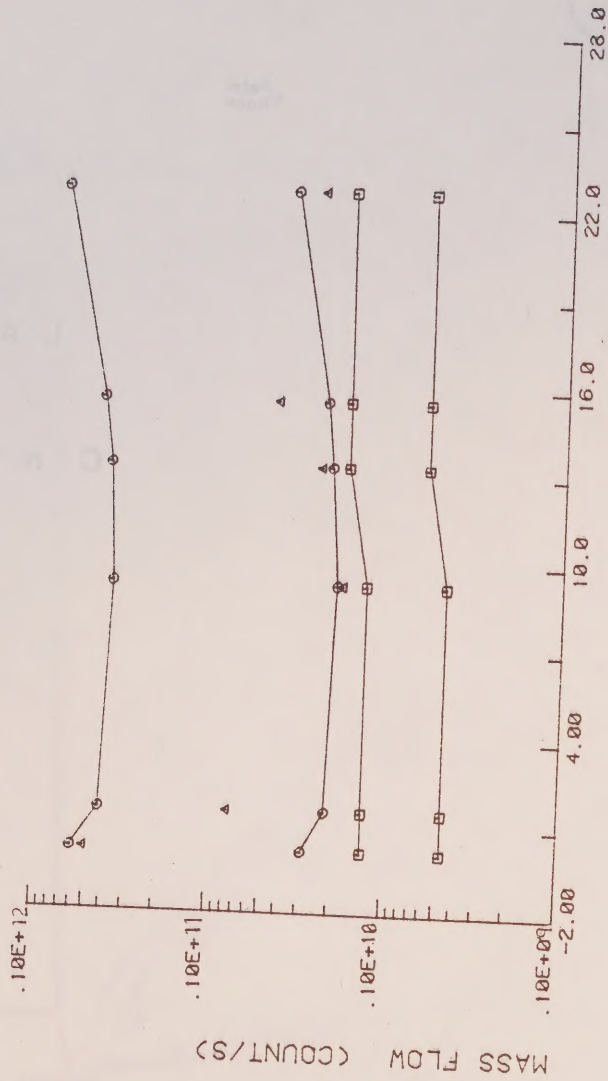




Figure 4

THAMES RIVER CL-OFF
TOTAL COLIFORMS - SUMMER



BEAK CONSULTANTS LTD T3692
ONTARIO MINISTRY OF ENVIRONMENT

FIGURE 5

GRAND RIVER
CL - ON
FECAL COLIFORMS -- SUMMER

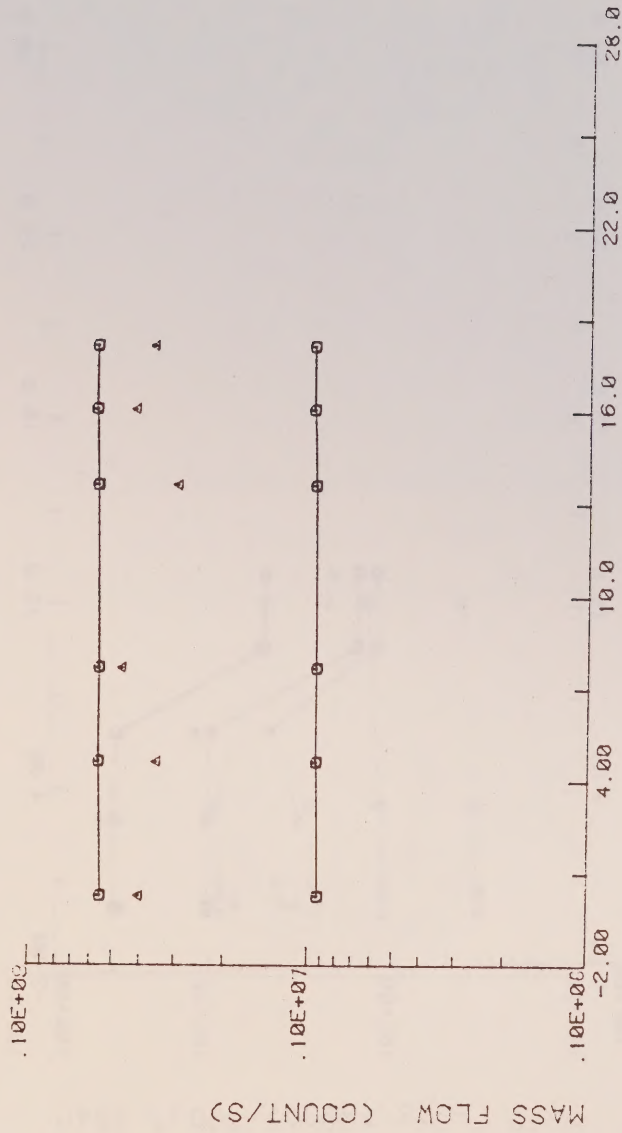
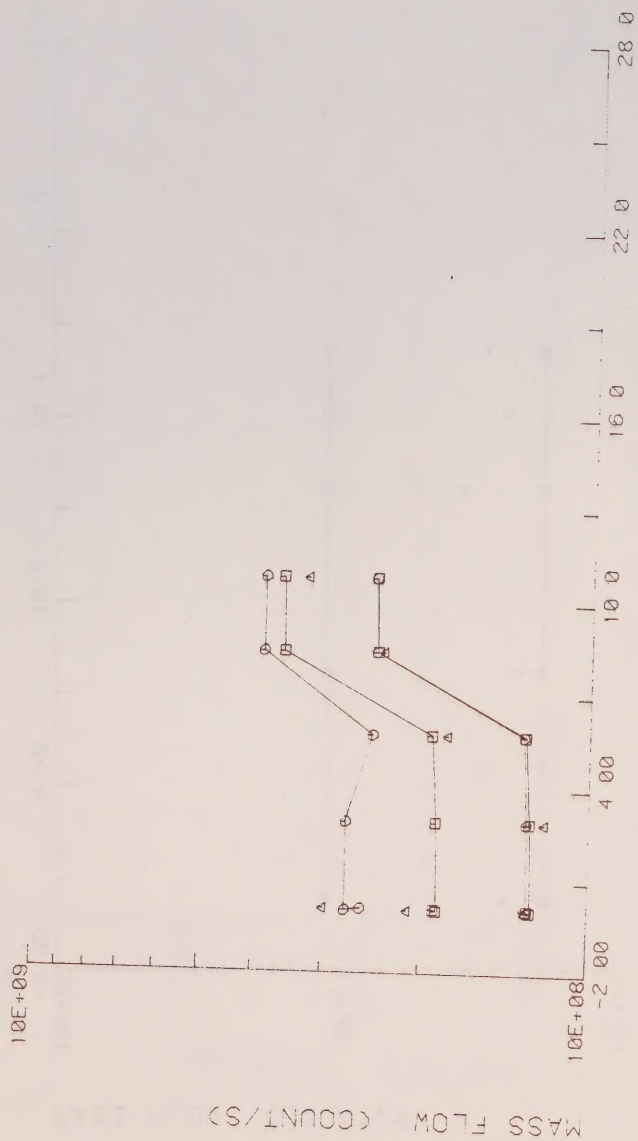


FIGURE 6

TIME OF TRAVEL (HRS)
BEAK CONSULTANTS LTD T3692
ONTARIO MINISTRY OF ENVIRONMENT

THAMES RIVER CL-OFF
KLEBSIELLA -- FALL



TIME OF TRAVEL (HRS)
BEAK CONSULTANTS LTD T3692
ONTARIO MINISTRY OF ENVIRONMENT

FIGURE 7

OTONABEE RIVER CL-OFF
FECAL STREP - SUMMER



TIME OF TRAVEL (HRS)
BEAK CONSULTANTS LTD T3692
ONTARIO MINISTRY OF ENVIRONMENT

FIGURE 8

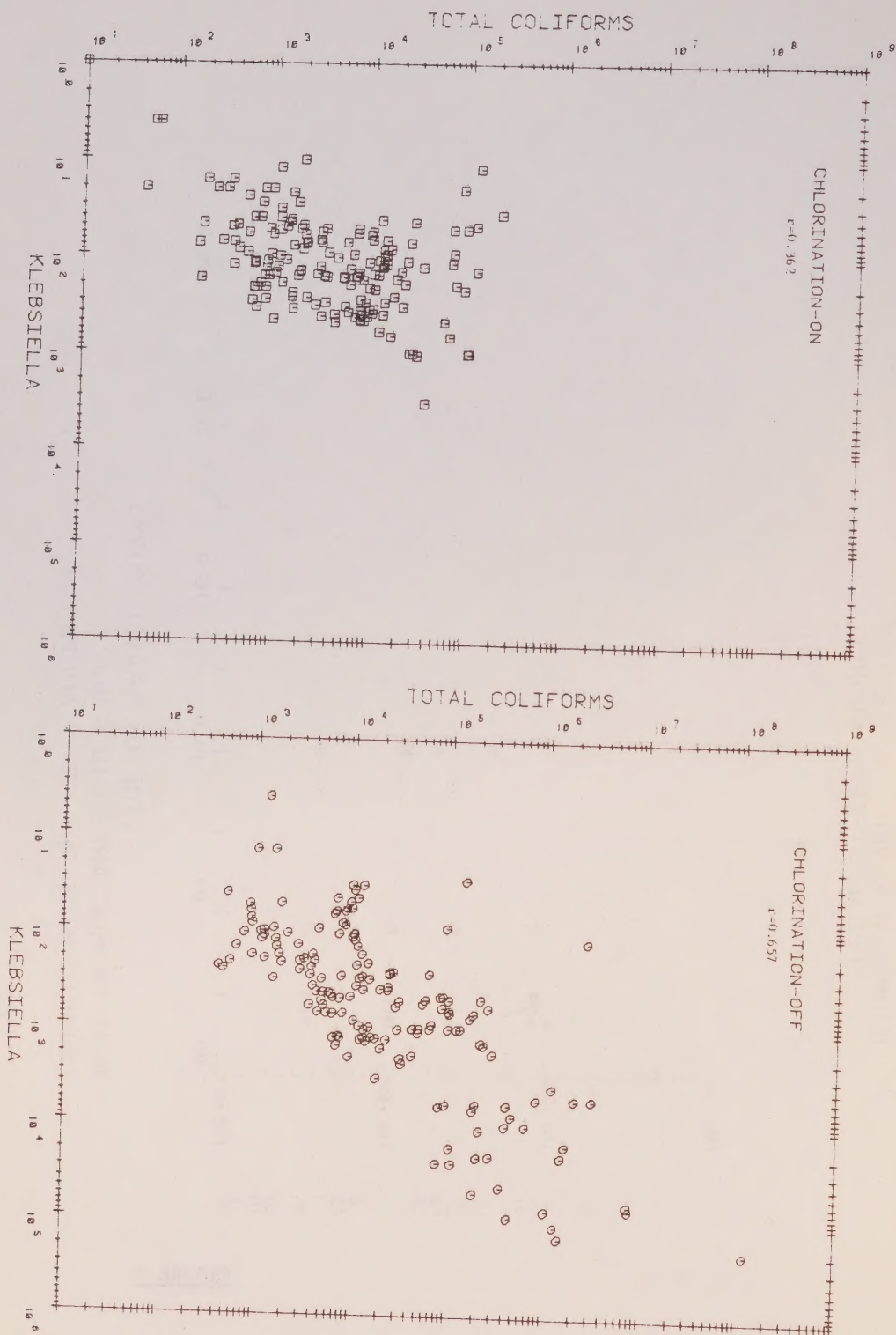


FIGURE 9

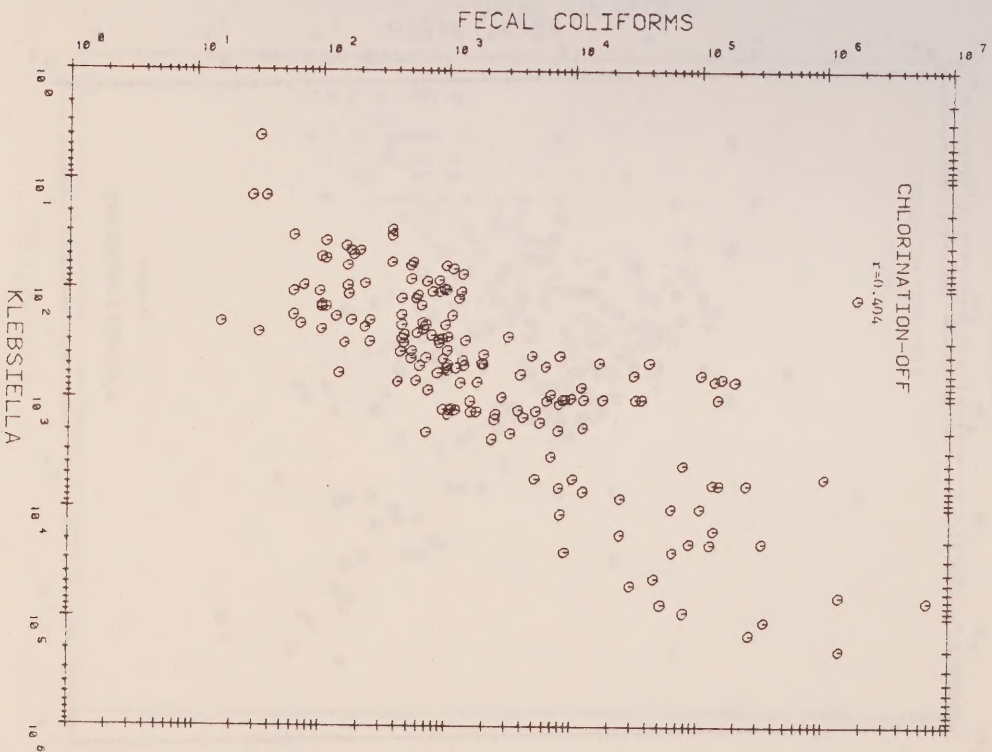
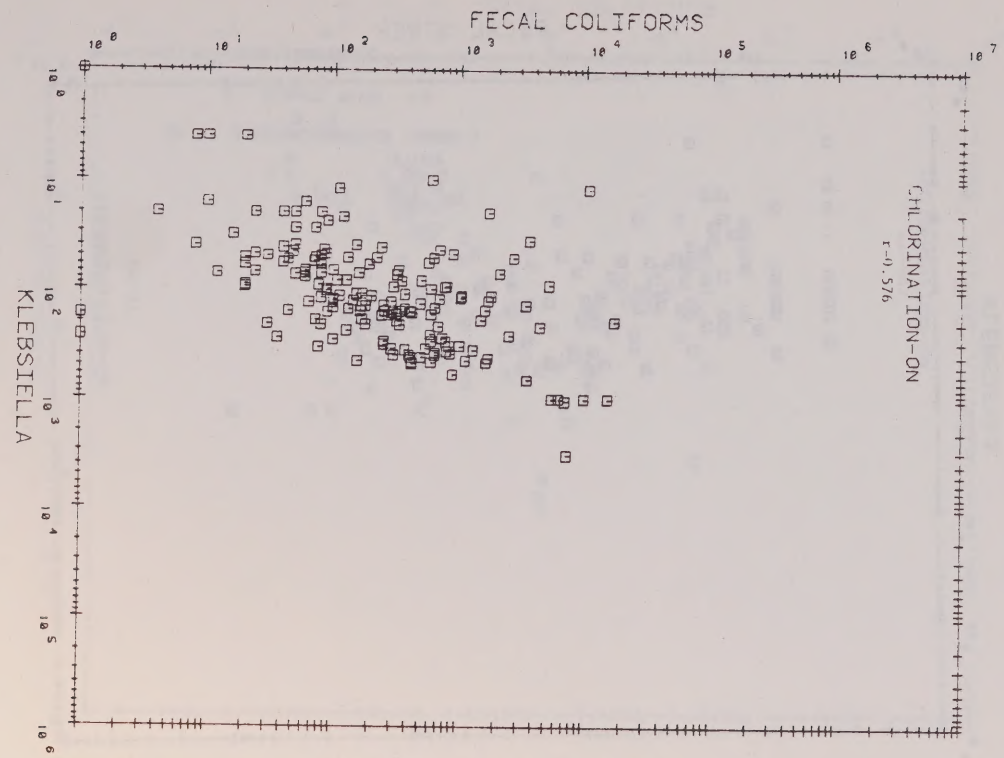


FIGURE 10

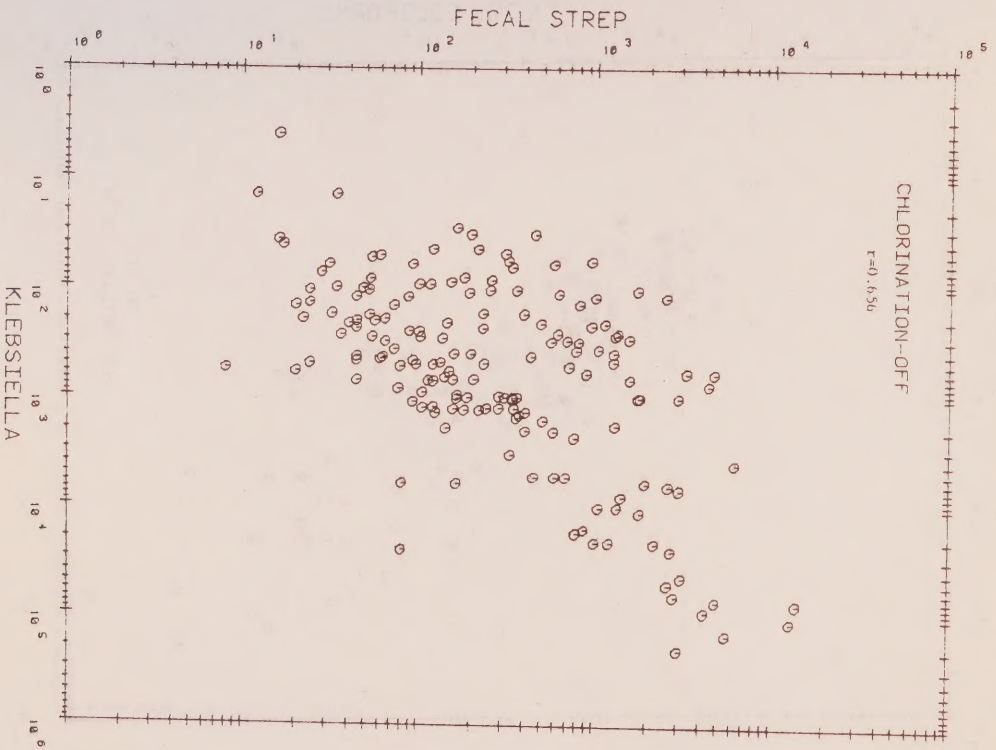
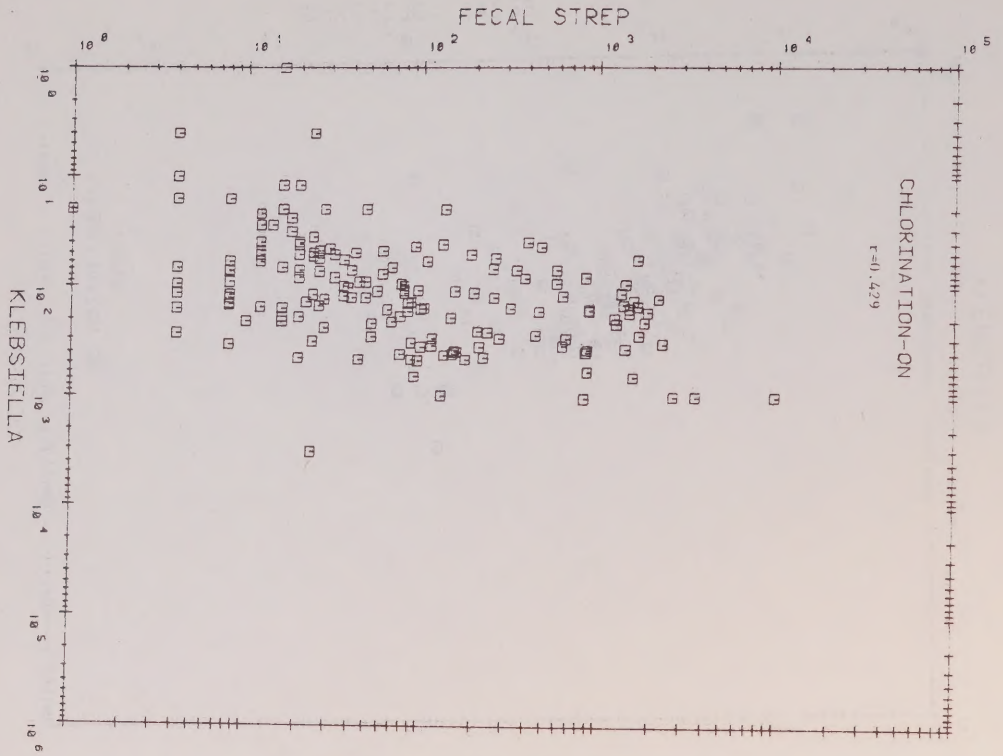


FIGURE 11

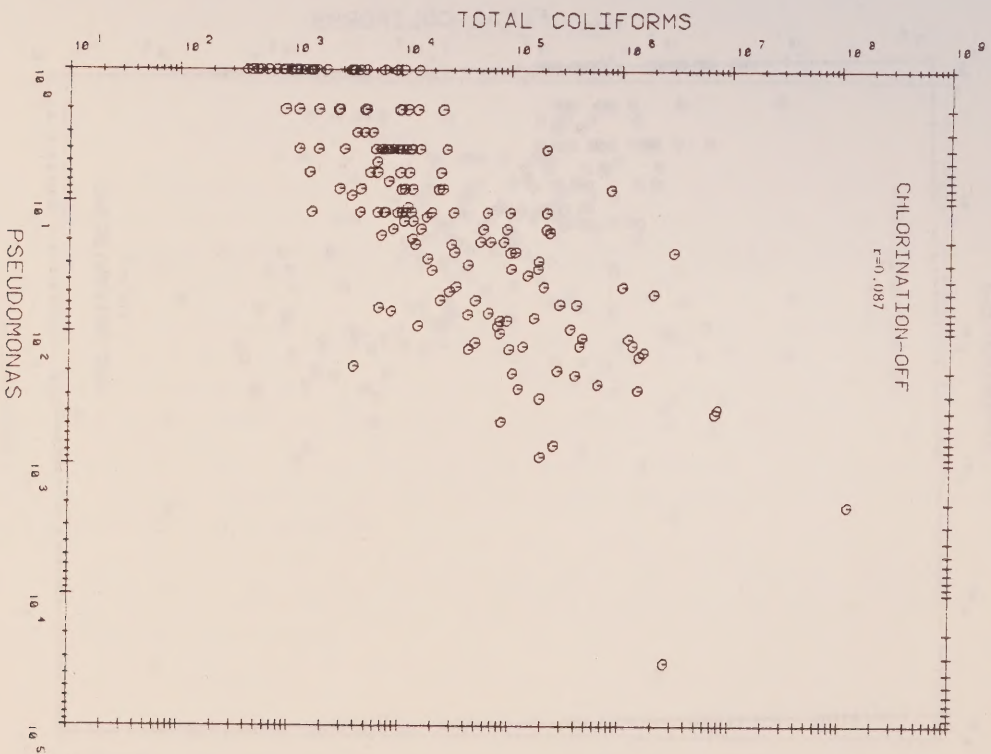
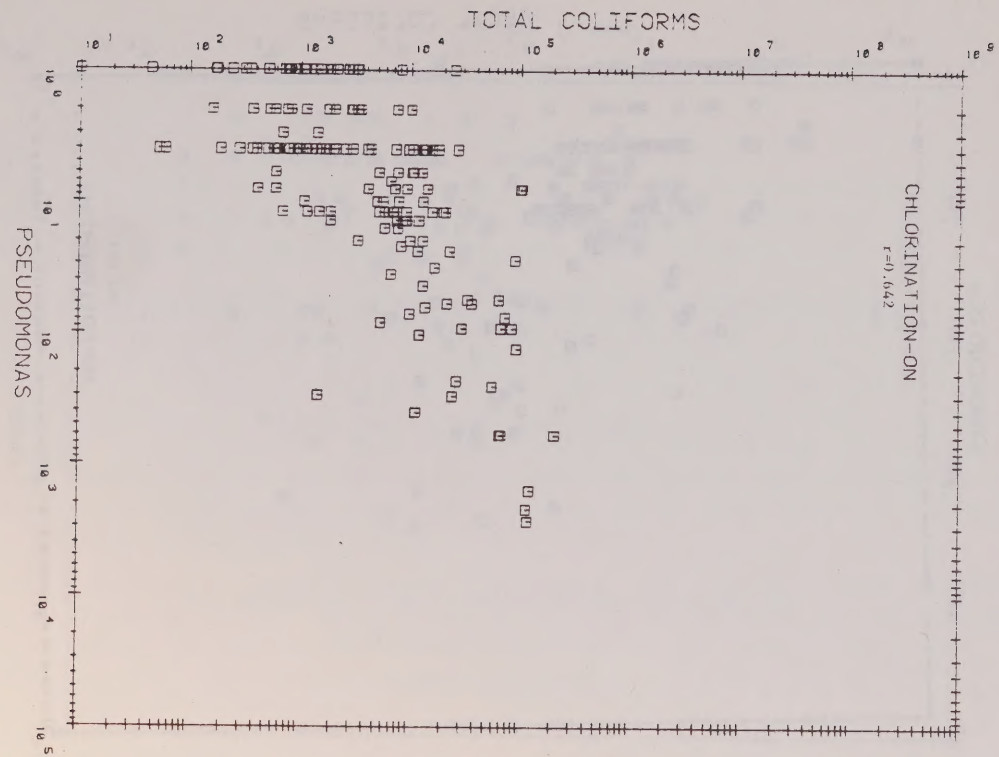


FIGURE 12

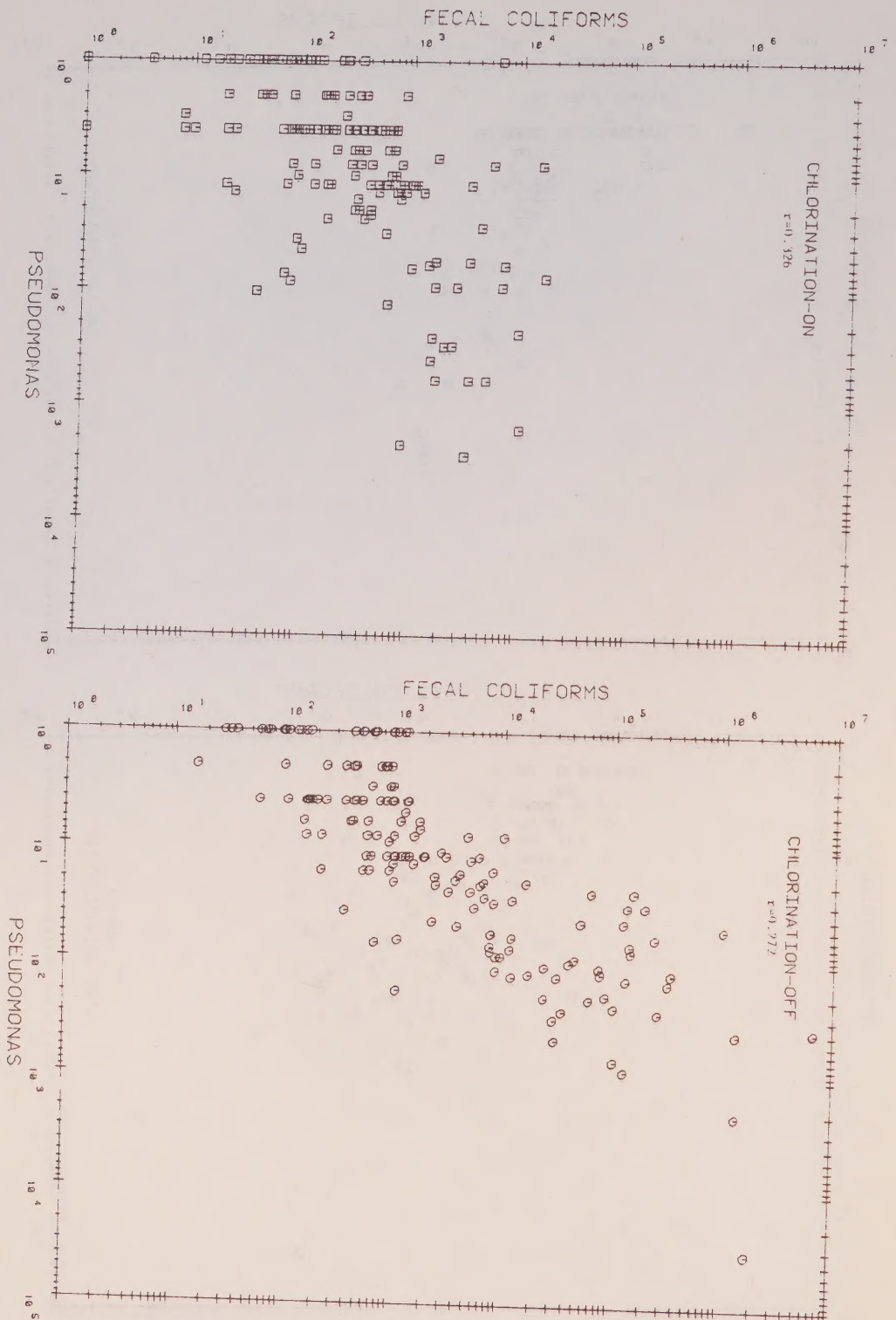


FIGURE 13

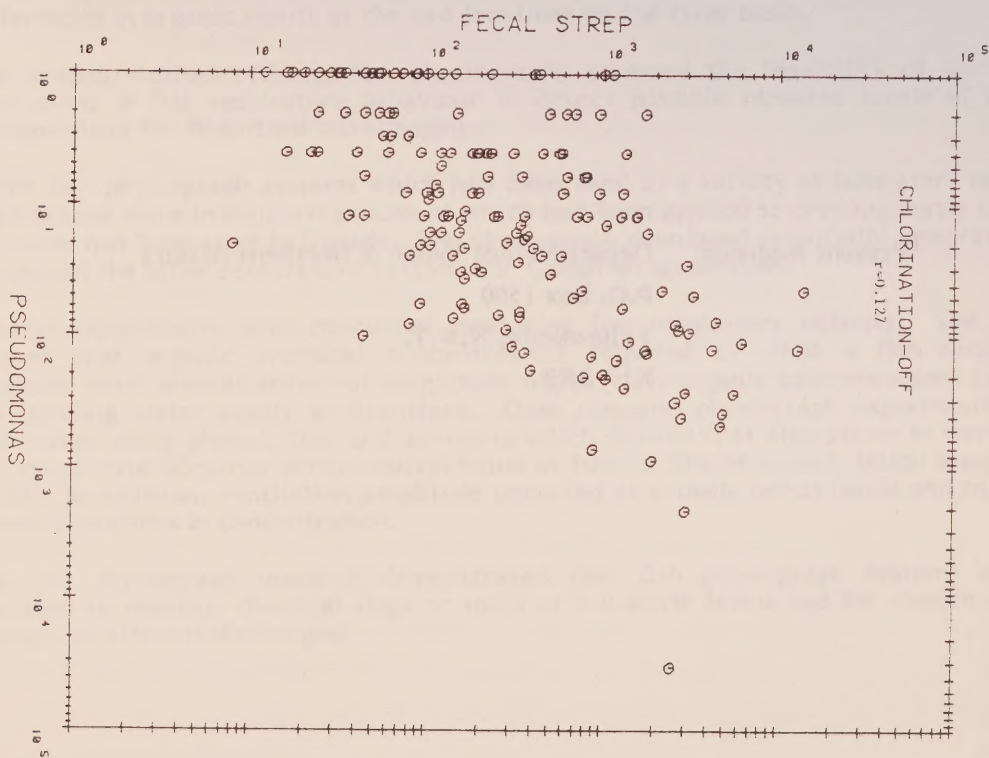
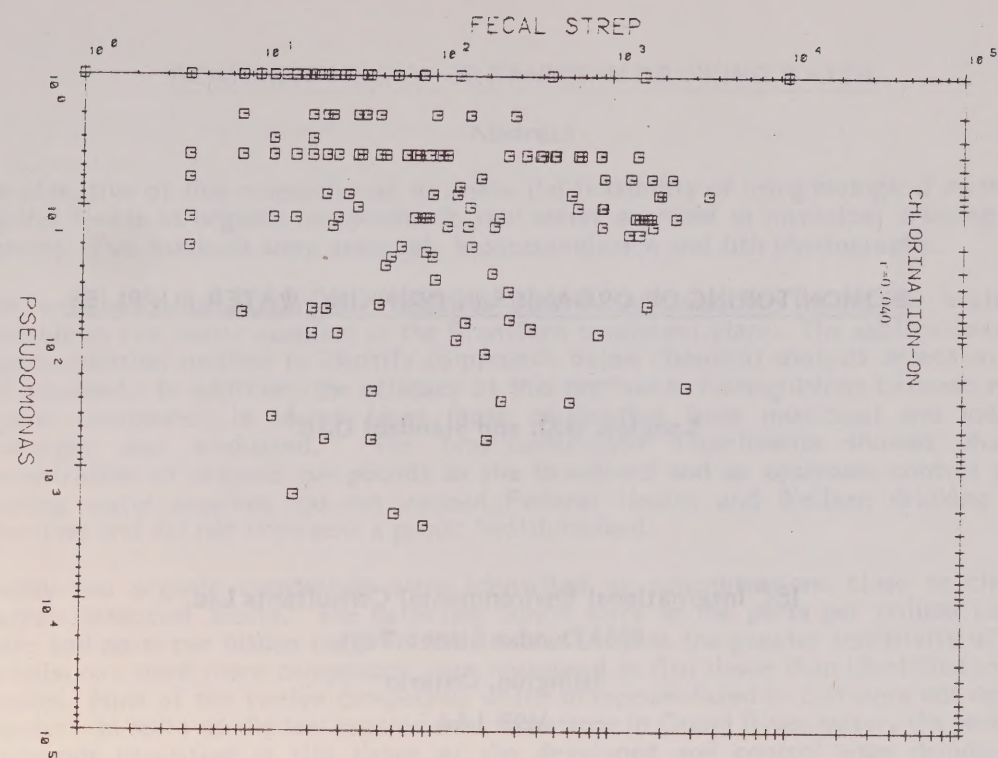


FIGURE 14

BIOMONITORING OF ORGANICS IN DRINKING WATER SUPPLIES

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BIOMONITORING OF ORGANICS IN DRINKING WATER

Abstract

The objective of this research was to assess the feasibility of using biological methods to monitor levels of organic compounds in raw water supplied to municipal drinking water systems. Two methods were assessed: bioaccumulation and fish physiography.

Fish were used to accumulate organics potentially hazardous to human health and available in raw water supplied to the Brantford treatment plant. The application of this bioaccumulation method to identify compounds below chemical analysis detection limits was assessed. In addition, the efficacy of this method in distinguishing between natural organic compounds in water from those originating from municipal and industrial discharges was evaluated. The bioaccumulation experiments showed that the concentration of organic compounds in the Brantford and an upstream control station drinking water supplies did not exceed Federal Health and Welfare drinking water objectives and did not represent a public health hazard.

Twenty-two organic compounds were identified at concentrations close to chemical analysis detection limits. The detection limits were in the parts per trillion range in water and parts per billion range in fish tissue. Despite the greater sensitivity of water analysis, one third more compounds were measured in fish tissue than identified in water samples. Nine of the twelve compounds which bioaccumulated in fish were not detected in water. In spite of the low organic concentrations in Grand River water, the levels and compounds identified in fish tissue at the developed and control sites demonstrated differences in organic inputs at the two locations on the river basin.

The second method utilizing fish physiography assessed the feasibility of monitoring alterations in fish respiratory behaviour to detect possible elevated levels of organic compounds in the Brantford water supply.

Seven fish physiograph systems which had been used in a variety of laboratory research applications were investigated; none of which had been applied to drinking water supplies and none had been used in Canada. The physiograph developed essentially integrated and optimized the other researchers' systems for Canadian application.

Several experiments were conducted measuring fish respiratory activity. The results showed that organic chemical concentrations required to elicit a fish respiratory response were several orders of magnitude higher than organic concentrations found in the drinking water supply at Brantford. Dose response physiograph experiments were undertaken using phenol, zinc and ammonia which showed that alterations in ventilation and cough rate occurred within several hours at 10% to 50% of acutely lethal levels (96 h LC50). In addition, ventilation amplitude occurred at acutely lethal levels and following severe elevations in concentration.

The fish physiograph research demonstrated that fish physiograph systems may be operated to monitor chemical slugs or spills at sub-acute levels and for monitoring the toxicity of effluent discharges.

INTRODUCTION

Raw water supplied to municipal drinking water systems contains a variety of natural and synthetic organic compounds. Recent advances in analytical technology have enabled the measurement of many compounds previously unidentified in water. Some of these organics which are found in parts per trillion levels may pose a hazard to public health, create taste and odour, taint fish and may be toxic to aquatic life.

In order to minimize introduction of man-made organics to water, wastes from municipal and industrial sources are treated prior to release into receiving waters. However, small amounts of synthetic organics may pass unchanged through the treatment process. As a result, monitoring of rivers at points of treated effluent discharges and downstream at areas of water use is needed to establish organic inputs to drinking water treatment plants.

At present, water quality monitoring and characterization is performed principally by physical and chemical methods. These methods do not provide continuous surveillance as sampling is infrequent. Also, technical and economic considerations limit the number of compounds which are measured. Thus, compounds which may be hazardous in water may occur undetected. Furthermore, the full potential of these materials to cause harm has not been established and complete toxic interaction between compounds has not been assessed.

In contrast, monitoring methods using living organisms such as fish can assess toxicity of substances in water. Fish maintain a continuous presence in water and thus integrate the influences of all substances in their environment. This monitoring provides a direct measure of the impacts of water quality on fish thus providing an excellent monitoring technique. This approach, termed biological monitoring can be used to detect toxic organic compounds and their effects and thus monitor quality of drinking water supplies.

This paper briefly summarizes the results of a two year research program conducted by IEC International Environmental Consultants Ltd., Islington, Ontario for the Ontario Ministry of the Environment. The research was financed by the Provincial Lottery Fund. A 233 page report containing 250 references was prepared containing all results of the research and a discussion of their significance.

OBJECTIVES

The objectives of the research were:

1. To identify organic compounds, if any, which are present in raw drinking water and which are bioaccumulative in fish;
2. To distinguish naturally occurring organic compounds in raw drinking water from those originating from anthropogenic sources;
3. To evaluate the applicability of biomagnification for increasing the analytical sensitivity of measurement of organic compounds in raw public drinking water supplies; and
4. To assess the feasibility of using a fish physiograph to detect elevated levels of organic compounds in raw drinking water supplies.

APPROACH

The feasibility of two biological methods to monitor organics levels in drinking water supplies was assessed: one with long-term monitoring and abatement applications (bioaccumulation) and the other to serve as an alarm indicator of sudden, increases in organics levels (physiography). Fish were used as test organisms.

The Grand River Basin was selected as the study area (Figure 2.2). This 6,671 km² drainage basin flows into Lake Erie and forms the largest watershed in Southern Ontario. Six major urban and over twenty rural communities are located in the drainage basin, which has an estimated population of 600,000.

Brantford was selected as the experimental site for both the fish physiograph and bioaccumulation studies since the city is dependent on the Grand River as a drinking water source and treated municipal and industrial outfalls occur upstream of the Brantford water treatment plant intake. The control site for the bioaccumulation study was located at Shades Mill on Galt Creek, a small tributary which drains an undeveloped portion of the watershed and joins the Grand River at Galt, 25 km upstream of

Brantford. Galt Creek drains rural, agricultural and undeveloped wooded areas and has no known pollution point-sources. Available water quality data indicated that the organic levels in Galt Creek were low and usually below detection.

The Brantford Water Treatment Plant drawing from the Grand River was selected as the downstream experimental site. The location was chosen as it is situated downstream of diffuse and point source discharges arising from four major urban industrialized areas. Also, taste and odour complaints have been periodically registered concerning the Brantford potable water supply.

This paper discusses the materials, methods, results, and conclusions of the bioaccumulation research first.

BIOACCUMULATION MATERIALS & METHODS

Laboratories were constructed at both sites for the fish exposure facilities (Figures 3.2 and 3.3). Each laboratory was capable of providing a continuous flow (10 L/min) of temperature controlled and aerated water drawn from the water supplies without retention or dilution. To minimize leaching or dissolution of substances into the water or sorption of organics from the water, all materials which contacted the exposure water were made of degreased iron, glass or perfluorocarbon plastics. Loss of trace amounts of volatile organic compounds through aeration of the exposure water was minimized by cascading the water between head-tanks instead of using bubblers. This also alleviated possible supersaturation of the water with gases following heating.

Online water monitors provided continuous measurement of turbidity, conductivity, dissolved oxygen, pH and temperature at the two sites. Fail-safes protected against loss of fish through power failure, variation in water temperature or changes in flow. Activation of the fail-safes triggered flow shut-off valves and simultaneously activated oxygen flow from compressed gas cylinders to the exposure tanks to maintain the level of dissolved oxygen.

The experimental design involved simultaneous exposure of one to two gram rainbow trout fry to untreated municipal water at the upstream reference and the downstream experimental site for a 12 week period. Specially formulated purified trout food was prepared to avoid potential organic contamination. Fish were collected for organic residue tissue analysis at both sites for weeks 0, 1, 2, 4, 8 and 12 of the exposure. During

the experiment, accumulator resin cartridges were installed at each site to concentrate organics from the water for subsequent organic analysis to compare organic levels in water with the organic levels and compounds accumulated in the trout.

Five hundred trout fry were held in each of four 100 litre aquaria at each site. Temperature control was maintained to ensure that fish at the two sites bioconcentrated the organics at the same rates relative to ambient levels and that bioconcentration occurred at a reasonable rate since the process is closely associated with the metabolic regime of fish. Each aquarium received a constant flow of water at 1.75 L/min which provided a 95% molecular replacement time of three hours. During the experiment the fish were fed the semi-purified diet twice daily at both sites at a daily rate of 4% of wet body weight. Incandescent lighting simulated a natural 10 h day/14 h night photoperiod. Black shrouds of plastic surrounded the exposure tanks to minimize disturbance.

During the experiments, exposure water was passed through cartridges (Amerlite XAD-2) at a rate of about 15 ml/min. The resin cartridges were renewed at both sites every 1 to 2 weeks. Synchronization of cartridge replacement with fish sampling was maintained. Following removal of a cartridge, the resin was removed from the column into solvent washed jars with teflon cap liners and then covered with acetone. The glass fiber material used to confine the resin in the cartridges was also stored in jars under acetone. These samples were refrigerated and stored in the dark until analyzed by the Ontario Research Foundation. In addition, water samples were collected throughout the experiment in acid-washed polyethylene bottles for anion and cation analysis.

BIOACCUMULATION RESULTS

Bioaccumulation may be broadly defined as the net accumulation of chemical residues in tissue, and it occurs through two pathways: bioconcentration, or direct partitioning from water, and biomagnification or accumulation from dietary sources. Previous field and laboratory studies have indicated that bioconcentration is the major pathway of bioaccumulation whereas, biomagnification appears to be important to body burden accumulation for compounds that are highly persistent in fish such as DDT or when levels in the water are low.

Fish have been demonstrated to accumulate organics in tissue at levels higher than those in water. In some cases the accumulation is 10^6 fold (from ppt in water to ppm in the

tissues). DDT, BHC and dieldrin are known to accumulate in fish and human tissues and therefore can be used as indicators and monitors of organic contamination. Fish not only accumulate organics to detectable levels but also screen organics according to their biological activity and likelihood of becoming cumulative poisons.

A number of general comments may be made concerning the bioconcentration process. Laboratory studies have shown bioconcentration to occur rapidly in most cases. Fish continuously exposed to a constant organic concentration usually reach a steady state body burden within ten days and maintain the equilibrium unless there is a change in the exposure. Transfer of contaminated fish to clean water results in rapid elimination of most compounds with resultant biological half-lives of less than seven days. However, organochlorine compounds that are highly lipophilic and nonreactive take longer to reach equilibrium and to be cleared from the body. These bioconcentration procedures are used to estimate the bioconcentration factor of a compound, expressed as BCF, which is the measured concentration of the chemical in fish tissue at equilibrium divided by the measured concentration of the chemical in water during the exposure. Evidence has indicated that the time to reach equilibrium, biological half-life and BCF are independent of exposure concentration.

Chemical analysis of water and tissue by capillary GC/EC was carried out by ORF for 27 organic compounds. Triazines and organophosphates were analyzed by packed column GC/N-P. Table 1 summarizes several of the principal organic residues analyzed in fish tissue samples and Table 2 summarizes the water sample analyses. Although the tables do not present all the chemical analyses, twenty two organic compounds were identified in fish or water samples.

These included six OC pesticides, five PAH's, six chlorobenzenes, two chlorophenols, one triazine herbicide, one phthalate ester and PCB. Of these, fifteen were identified in fish and ten in water representing 30% and 20% respectively of the total number of organics analyzed. The concentrations of organics identified in fish or water were at levels near detection limits: ppt in water and ppb in fish tissue. No organo-phosphorus pesticides, phenoxy herbicides and aliphatic, alicyclic or aromatic organo-halogen compounds were detected in either water or fish.

Based on a five fold increase in fish weight over the 12 week period increased body residue suggested bioaccumulation of BHC, dieldrin, PCB, several chlorobenzenes, chlorophenol, fluoranthene and benz [a] anthracene. In this evaluation, minimum detectable amount was used for the week 0 tissue concentrations when levels were below detection. Absence of these organics in fish food and in baseline (week 0) fish tissue further substantiated bioaccumulation. Only the PAH's fluoranthene and benz[a] anthracene were detected in fish food as well as water and thus some of the accumulated residues for these compounds may have originated from food rather than the water. Some DEHP measured in the fish and resin samples is suspected to have arisen from contamination by plastics used during the chemical analysis. For example, the resin blank contained high amounts (24 ug) of this widely-used plasticizer.

The number of organics bioaccumulated in the fish increased with length of exposure so that by the twelfth week twelve compounds had bioaccumulated compared with two and six compounds at exposure weeks 2 and 8 respectively. A longer exposure may have resulted in further bioaccumulation of some of the more persistent and lipophilic organics.

Comparison of tissue residue data for week 12, at Brantford and Shades Mill showed higher levels for Brantford than Shades Mill for 13 of the 15 compounds identified. Five of these compounds were not detected in fish at Shades Mill. This probably reflects the municipal and industrial discharges which exist upstream of Brantford which are not present at Shades Mill.

Ten organic compounds were identified in water samples. Six of these compounds, the two chlordane isomers, atrazine and three PAH's were detected in water but not found in fish. This was not unexpected for atrazine, due to its low residue-forming potential. Chlordane, on the other hand, is highly bioaccumulative but was detected in both the particulate glass wool sample and the resin and may have been adsorbed on particles and unavailable to the fish. The atrazine level of 35,000 ng for the 100 L of water extracted was the highest level detected and may be typical of water draining a corn producing region.

The Brantford water sample for week 2 was collected during runoff and snowmelt. It was anticipated that the increased solids loading might carry coincidentally higher organic content. The results did not show an increase during runoff in the fish or in water.

BIOACCUMULATION CONCLUSIONS

In spite of the low organic concentrations in water, the levels and compounds identified in fish tissue at the developed and undeveloped sites clearly demonstrated differences in organic inputs at the two locations on the river basin. By exposure week 12, fish at the site located downstream of treated industrial and municipal discharge areas showed higher levels for 13 of the 15 compounds identified, five of which were not detected in fish at the upstream reference site. As the fish exposure progressed, the number of compounds demonstrated to bioaccumulate increased and the tissue concentrations increased. A longer fish exposure may have increased bioaccumulation of the more lipophilic and stable organics. However, the research was not designed to monitor for an extended period.

Finally, none of the organic residue concentrations detected in fish tissue approached guidelines restricting fish consumption and the levels in water were within Federal drinking water guidelines.

FISH PHYSIOGRAPH MATERIALS & METHODS

Biological monitoring, used in conjunction with physical-chemical determinations, has potential as an early warning tool. Subtle changes in water quality may be detected by monitoring the response of test fish which continuously integrate the effects of all parameters. However, not all biological monitoring methods are suitable for such a program. Traditional means of monitoring such as biotic index assessment and acute and chronic toxicity testing are inappropriate primarily due to test time.

Research has shown that monitoring methods using fish respiratory parameters are among the most sensitive. Signs of respiratory impairment appear during exposure to sublethal contaminant concentrations and within sufficiently short periods to enable remedial action. Changes in respiratory rate, increased gill purge response and changes in depth of respiration; unlike various behavioural or locomotory responses, monitor the strength of the stimulus, and can be measured and quantified electronically.

This research presents the preliminary development of such an early warning system to detect elevated levels of organics in water. The research included a review and evaluation of previous fish physiograph systems, the set-up and testing of a hard copy

system in a practical field situation and the results of the first dose-response applications in Canada. The installed system was the first ever installed to monitor a public water supply.

The first phase of the study included a detailed review of seven previous physiograph systems as background for design of the experimental unit followed by its set-up, calibration and tuning. Experiments were then undertaken to determine if changes in fish activity occurred during exposure to the untreated drinking water.

A hard copy recording system was used to enable full inspection of the respiratory waves so that several respiratory parameters could be assessed and a stable, predictable output could be established. This was a necessary step if the system was to be computer automated later for practical monitoring. Electrodes, electrode chambers and amplifier/filters compatible with an automated approach were used.

The procedure involved a step-wise approach to continuously improve the sensitivity of the physiograph. The approach incorporated a feed-back loop for the readjustment of the monitor/alarm to tune the system specifically to organics.

The fish physiograph system operated in the following manner: free-swimming fish were confined individually in monitoring cells. The microvolt bioelectric potentials emitted as they respired were received by two submerged hard wire electrodes affixed to the ends of the holding cells and were carried along shielded conductors to high gain frequency selective amplifiers and frequency filters for processing. At designated intervals, a mechanical switching device or programmed multiplexer passed the amplified signals to a hard copy recording system for manual interpretation of the complete respiratory waves. The final system selected is depicted in Figures 4.10 and 4.11. The Virginia Polytechnic Institute and State University system was selected. Its advantages were commercial availability, documented capabilities and incorporation of a hard copy system as well as computerized capability. The hard copy portion of the VPI and SU system was proposed for the first phase of this study and if the feasibility of drinking water monitoring could be demonstrated, continuous monitoring could be achieved by adding on a computer interface for future research.

The system consisted of 8 electrode chambers. Each chamber held one free-swimming fish (Figures 4.12 and 4.13). The chambers were contained in a vibration and sound proof

enclosure equipped with artificial lighting, simulated photoperiod and tubes to feed the fish. A stainless steel electrode was attached with silicone sealant to each of the two end plates of the electrode chamber for signal reception. Mueller alligator clips soldered to the two conductors of the Belden shielded cable were attached to the wire electrodes.

The electrode signal was transmitted along the shielded cable through an electro-magnetic double-throw relay controlled by a continuous cycling two circuit timer to the amplifier/filters designed and built by VPI and SU. The Potter Brumfield relay and Cramer timer enabled the monitoring of eight fish on the four channel strip chart by selecting the fish by banks of four. Following processing, the signals were transmitted to a 4-channel Hewlett-Packard 7414A polygraph equipped with 8803A preamplifiers and recorded.

The biomonitoring facility was located close to the Brantford raw water intake. The test laboratory was contained in a 4.6 m x 3.1 m room within the WTP. The laboratory water was drawn directly from the intake canal with no retention or dilution to assure detection of potential short-term changes in water quality. Automatic in-line monitors provided hourly measurements of water temperature, dissolved oxygen, pH, turbidity and conductivity. Monitor alarms were also used in this portion of the study.

Experiment 1

In the first experiment, the respiratory activity of largemouth bass was recorded for a one week period while exposing the fish to the intake water. The experiment was to test the hard copy recording system for reliability under continuous use, to examine variation in fish respiration in a practical situation, to determine the time needed for fish to stabilize activity following transfer to the exposure chambers, and to assess the effect of a controlled dose of chloroform on fish respiration.

Largemouth bass (weight of 17 ± 3 g) were transferred to four electrode chambers following three weeks acclimation to the 20°C incoming river water. Respiration of each fish was then monitored for five consecutive minutes at two hour intervals throughout the seven day exposure.

Dissolved oxygen, pH, temperature, conductivity and turbidity of the water was recorded on punch tape of the robot water monitoring unit every hour during the same 5 minute

interval as the physiograph recordings. Calibration of physico-chemical monitors was checked daily. An artificial 9h day/15h night photoperiod was maintained during acclimation. Half hour light dimming and brightening occurred at 1700h and 0700h, respectively simulating dusk and dawn periods. The experimental fish were fed live meal worms *ad libitum*. Cell flow rate of 600 ml/minute ensured a 95% molecular replacement time of less than 1/2 hour. On exposure day 5, dosage of one of the fish with 3.25 mg/l of chloroform was initiated and continued for 40 hours.

Experiment 2

In the first experiment, the reliable production of clean, stable signals proved the physiograph amenable to computerization for real-time monitoring. However, before interfacing the physiograph to a computer, its ability to respond to elevated levels of organics had to be demonstrated as elevated levels had not been encountered in Grand River water. Manual data interpretation to determine changes in signals associated with the response of fish to changes in water quality was required prior to automating the monitoring system.

Based on the absence of any significant changes in fish activity or water quality in the first experiment and to maximize data obtained on the physiograph's capabilities, a second experiment incorporated dose-response trials and monitored the raw water. The dose-response experiments assessed the system's ability to respond to elevated levels of substances in the raw water. Control cells exposed to raw water served as monitors of raw water and also as references for the dose-response cells to confirm stress detection. Simultaneous water sampling and analysis were conducted for compounds in the control and dose-response cells.

The dose response compounds were phenol, ammonia and zinc. These compounds may occur in municipal and industrial discharges and may pose health hazards and create taste and odour.

The exposure test, including a six day acclimation period, lasted 22 days. Two fish were exposed to each of the three compounds and two fish served as references. The compound concentrations were selected to encompass reported values known to elicit a respiratory response. The concentrations were increased sequentially simulating a chemical spill upstream. Moreover, this approach ensured the fish had not been

previously exposed to a high concentration rendering them insensitive to subsequent exposures. The exposure to each concentration was usually 48 hours. When a response was observed, a washout recovery was followed by reexposure to examine if the response could be repeated. On the last two days of exposure, the two reference fish were spiked to provide additional data on sensitivity and respiratory response. These experiments used largemouth bass (weight of $4.4 \pm .5$ g) held for three weeks prior to introduction into the electrode chambers. The respiratory activity of each fish was monitored at 2 hour intervals during the baseline period and the subsequent 12 days of dose-response.

Phenol solutions were prepared from pure crystals. Ammonia was added as ammonium chloride and zinc solutions were prepared using zinc sulphate.

Dissolved oxygen, temperature, pH, conductivity and turbidity were monitored automatically on punch tape at hourly intervals during the 22 day experiment. Composite samples of raw water were collected daily in clean, solvent-rinsed glass bottles for organic analysis. The carboys were sealed with washed aluminum foil and stoppered. A subsample of each composite was collected for multi-element anion/cation scan.

The physiograph strip chart was manually analyzed for respiratory rate, cough frequency and amplitude of ventilation at the end of the experiment. Respiratory rate for each fish was plotted and correlated with chemical dose. The sensitivity of the polygraph system to both natural and artificial levels of the compounds was then determined.

PHYSIOGRAPH RESULTS & DISCUSSION

Experiment 1

The VPI and SU amplifier/filters were highly reliable and produced clear, stable signals throughout the test. Respiratory rate and amplitude of respiration varied considerably during the exposure and followed a diurnal pattern due to photoperiodism. Figure 4.14 is typical of the results obtained. However, coughs or gill purges were infrequent and showed no trend. The water quality was uniform during the experiment and precluded correlating fish activity to variations in water quality.

Abrupt changes in fish respiratory activity occurred following half hour light dimming and brightening. Amplitude of ventilation and ventilatory rate was greater during the day than at night.

Respiratory rates for the different fish were variable. For 75% of the time, variation in respiratory rates between fish at the same time of day was greater than for individual fish for different days but for the same time period. For light and dark periods, 52% and 91% respectively of the variances for respiratory rates for individual fish were less than those between fish. Therefore, comparison of a fishes own activity would narrow the limits defining abnormal respiratory activity and would increase the sensitivity of a monitoring system.

Based on the results of fish respiratory activity, there was no evidence to suggest that fish which had been exposed 3,250 ug/l chloroform altered activity from that prior to exposure to chloroform or from that of the reference fish. Since this chloroform concentration was an order of magnitude higher than the highest levels reported in raw or treated drinking water and above drinking water guidelines, it is unlikely that the fish physiograph could be used to monitor safe water quality in drinking water supplies.

Experiment 2

There was variation in the response of the test-fish prior to introduction of the three chemicals selected for the dose-response evaluation. Figures 4.18 illustrates the pre exposure variation up to the eleventh days when the fish was dosed with phenol. Similar variation was observed with other fish used in dose response experiments. This variation

was not attributed to a reaction to ambient levels of compounds occurring in the drinking water source but rather to inherent variation between and within fish. There was no correlation between fluctuations in respiration of the difference test-fish either to each other or to changes in the raw water as water quality was relatively stable throughout the experiments.

Some of the variation in the respiration was attributed to the diurnal pattern but this variation was less well-defined than in Experiment 1 where night respiration was less variable and lower than in the day. This disruption of the rhythm of the fish may have been caused by the lengthening of the night period to 18 hours. Also, the colder water in experiment 2 may have reduced the metabolic rate of the fish such that there was less clear active and quiescent periods.

Fish exposed to sublethal levels of stepwise concentration increments of phenol, ammonia and zinc significantly altered their respiratory activity. Ventilatory rate, cough frequency and amplitude of respiration were all affected by exposure to these introduced chemicals. Respiration changes occurred at fractions of levels acutely lethal to fish. High concentrations produced shorter response times such that respiration change due to acutely lethal concentrations occurred in less than two hours.

Exposure to 1.5 mg/l phenol provoked an increased cough frequency. Elevation of the concentration from 1.5 to 4.6 and then 7.9 mg/L resulted in a substantial rise in ventilation rate. Exposure to 22 mg/L phenol for a 1-5 hour period caused a significant decline in amplitude of ventilation followed by death.

The pattern of response to ammonia was different than to zinc and phenol. Initially, there was no cough response. Also, there was no increase in ventilation rate and there was a trend towards a slight decline in respiration. The most significant response was a change in respiratory pattern from the usual day and night pattern to one of multiple ventilations with extended apneic period of over 20 seconds between breaths. Also, amplitude of ventilation was elevated at exposures greater than 10 mg/l ammonia.

The detection limits and response times for the three compounds were similar to those reported by other researchers and the concentrations which elicited alterations in respiration were fractions of acutely lethal levels.

The most sensitive respiratory parameter was cough response. Ventilatory rate changes were noted at concentrations of 10 and 25% of the 96 hour LC50 for zinc and phenol, respectively. There was no cough response to ammonia, even at lethal exposure levels.

The capital cost of building a similar physiograph system, excluding the laboratory and auxiliary support equipment is estimated to be approximately \$10,000. The system components are available in Canada. The VPI and SU system which has minicomputer interface would cost an estimated \$25,000. However, the system developed on this research study could be interfaced with a less costly microcomputer for approximately \$13,000.

PHYSIOGRAPH CONCLUSIONS

The research and literature review has shown that organic chemical concentrations required to elicit a respiratory response by fish were several orders of magnitude higher than organic concentrations found in the drinking water supply at Brantford. Fish did not alter their respiratory activity to change in levels of organics at Brantford. However, fish respiration could be used to monitor organic levels if ambient concentrations are significantly higher than levels measured in the Grand River.

Dose-response experiments using phenol, zinc and ammonia showed that alterations in respiratory parameters occurred within several hours at 10-50% of acutely lethal levels (96 h LC50). Cough and ventilation rate were sensitive respiratory parameters. In addition, ventilation amplitude illustrated acutely lethal levels and severe elevations in concentration. Different compounds evoked different respiratory responses on the fish. Phenol and zinc which act directly on the gill membrane affected cough and ventilation rate while ammonia which interferes with gill physiology did not stimulate a cough response but altered the pattern of ventilation.

The research has shown that fish physiograph systems could be operated to monitor chemical slugs or spills at sub acute levels and for monitoring the toxicity of effluent discharges. Future research should consider automating the system with a computer for real time evaluation of the data.

CONCLUSIONS

- 1) In spite of the greater sensitivity of water analysis, one third more organic compounds were measured in fish tissue than water.
- 2) Fish exposed to Brantford intake water showed higher levels for 13 of the 15 compounds identified than at the upstream site.
- 3) Bioaccumulation correlated positively with fish exposure period.
- 4) Organic chemical concentrations in Brantford drinking water supply were below levels which would elicit a respiratory response by fish.
- 5) Fish could be used to monitor organic levels in water if ambient concentrations are significantly higher than in the Grand River, eg. a spill condition.
- 6) Dose response experiments with phenol, zinc and ammonia showed the sensitivity of the fish physiograph when respiratory pattern changed within a few hours at subacute levels.

Acknowledgements

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TABLE 1: SUMMARY OF ORGANIC RESIDUE LEVELS IN FISH TISSUE (ug/kg)

	Baseline Week 0	Shades Mill Week 12	Brantford Week 12
OC Pesticides			
BHC	N.D.	<10	20
Lindane	N.D.	N.D.	N.D.
Dieldrin	N.D.	<10	10
Mirex	N.D.	N.D.	N.D.
Chlorobenzenes			
1,2,4	N.D.	10	30
1,2,3	N.D.	<10	10
Chlorophenols			
2,3,4,5	N.D.	N.D.	40
Penta	N.D.	N.D.	N.D.
PCB Aroclor	55	50	60
Organo-Phosphates	N.D.	N.D.	N.D.
Phenoxy Herbicides	N.D.	N.D.	N.D.
Triazines	N.D.	N.D.	N.D.
PAH-Fluoranthene	3	1.4	4.5

TABLE 2: SUMMARY OF ORGANIC RESIDUES IN WATER (ng/100 ml)

	Brantford Intake
OC Pesticides	
BHC	N.D.
Lindane	N.D.
Dieldrin	112
Mirex	N.D.
Chlorobenzene	
1,2,4	N.D.
1,2,3	N.D.
Chlorophenols	
2,3,4,5	N.D.
Penta	625
PCB Aroclor	N.D.
Organo Phosphates	N.D.
Phenoxy Herbicides	N.D.
PAH-Fluoranthene	24

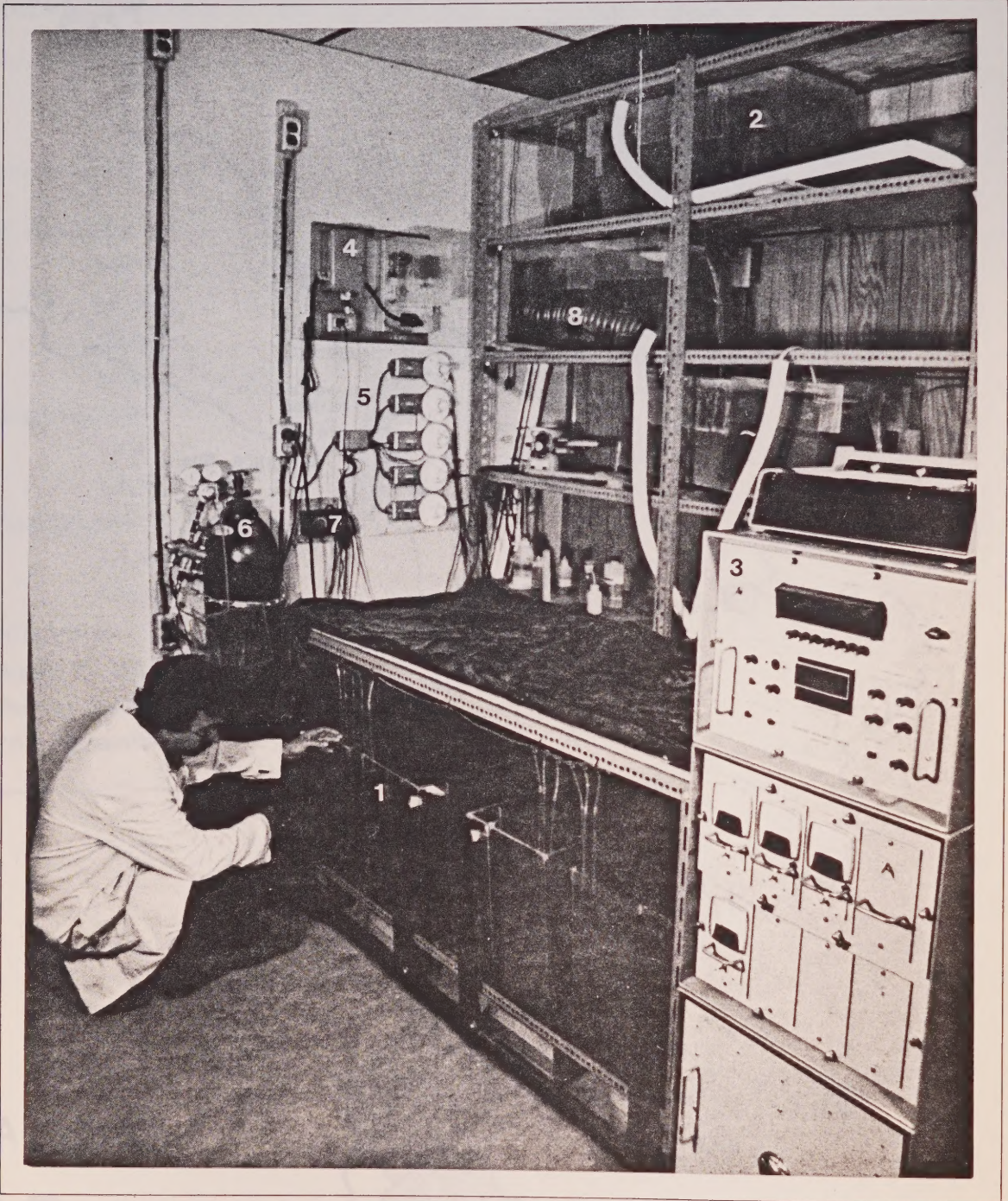


Study Area

2.2

Bioaccumulation Research Laboratory

3.2



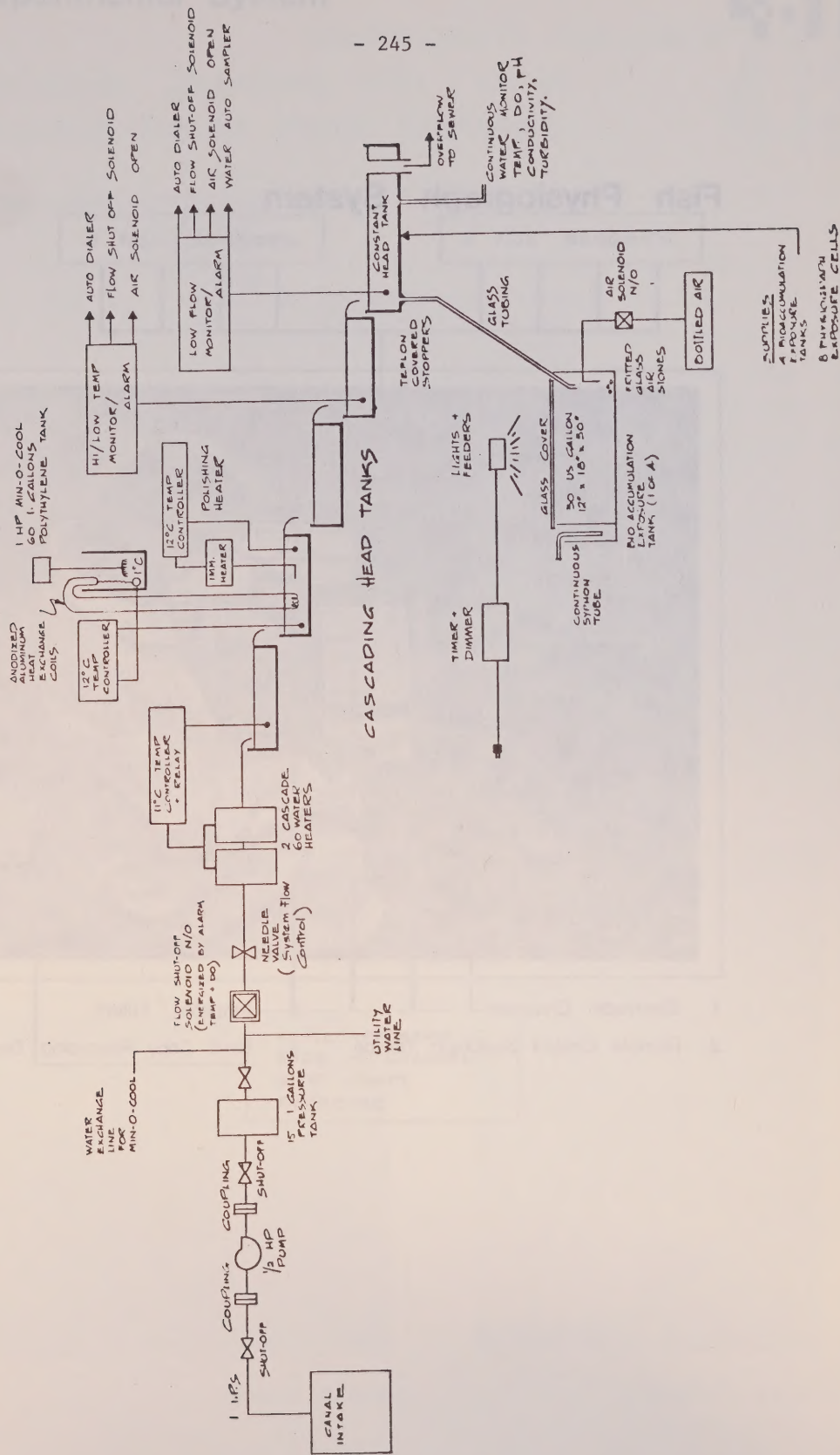
- 1 Bioaccumulation Exposure Aquaria
- 2 Cascading Head Tank
- 3 Continuous Physical / Chemical Water Monitor
- 4 Photoperiod Controlling Mechanism

- 5 Lighted Alarm Box
- 6 Emergency Compressed Oxygen Supply
- 7 Automatic Telephone Dialer
- 8 Water Cooling Coil

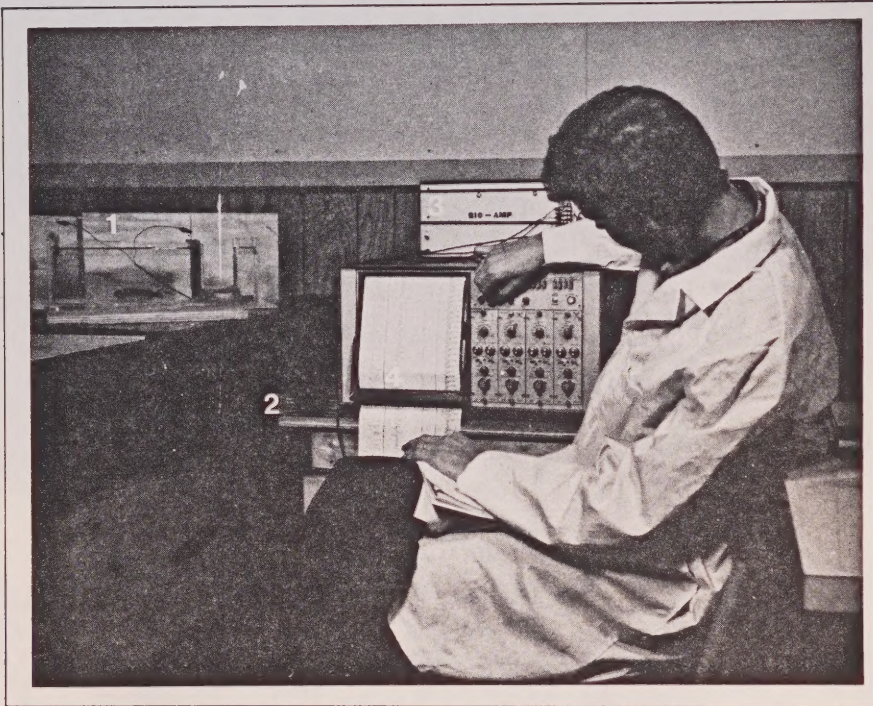
Lab Flow Plan

BRANTFORD

3-3

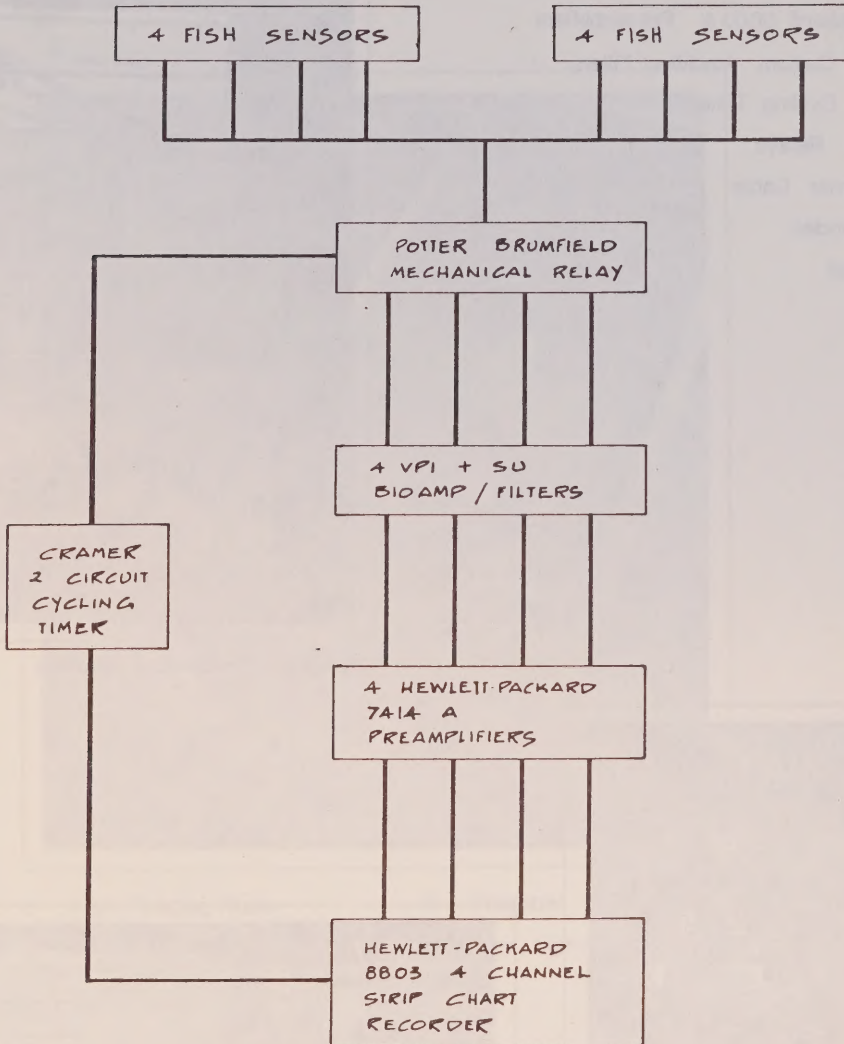


Fish Physiograph System



- | | |
|-----------------------------------|------------------------------|
| 1 Electrode Chamber | 3 Amplifier/ Filters |
| 2 Remote Control Switching Device | 4 Hard Copy Recording Device |

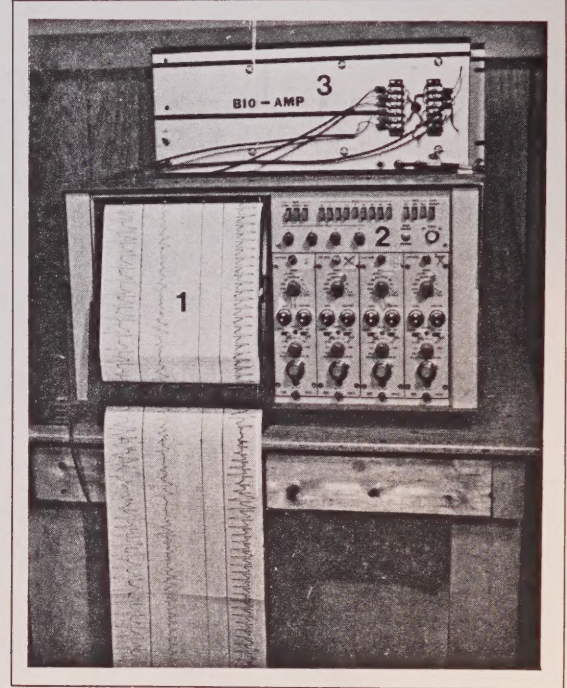
Experimental System



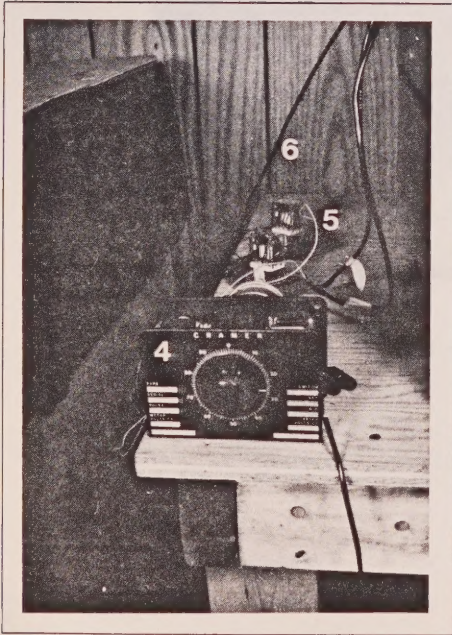
Fish Physiograph Components

4.12

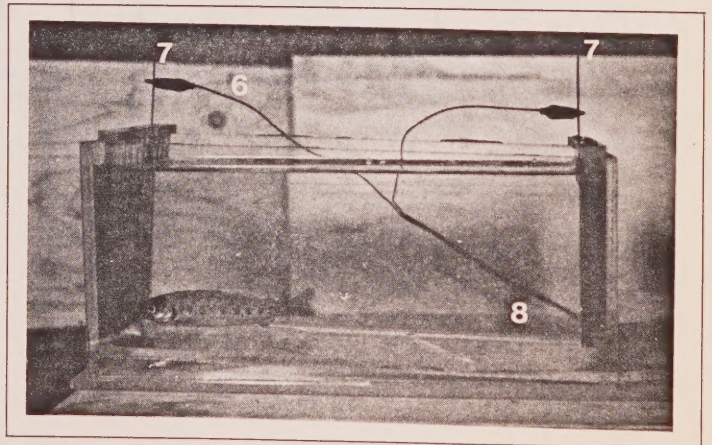
- 1 Hewlett-Packard 7414 A 4 Channel Polygraph
- 2 Hewlett-Packard 8803 A Pre-amplifiers
- 3 VPI & SU Custom Amplifier/ Filters
- 4 Continuous Cycling Timer
- 5 Mechanical Relays
- 6 Signal Carrier Cable
- 7 Wire Electrodes
- 8 Holding Cell



Biosignal Processing System



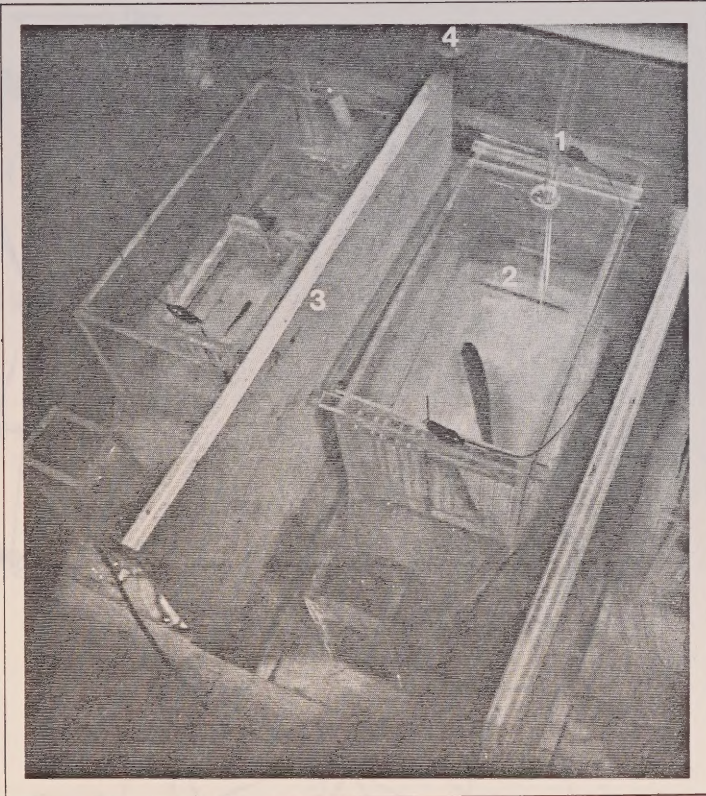
Switching Mechanism



Electrode Chamber

Electrode Chambers with Fish in Vibration/Sound Proof Enclosure

4.13

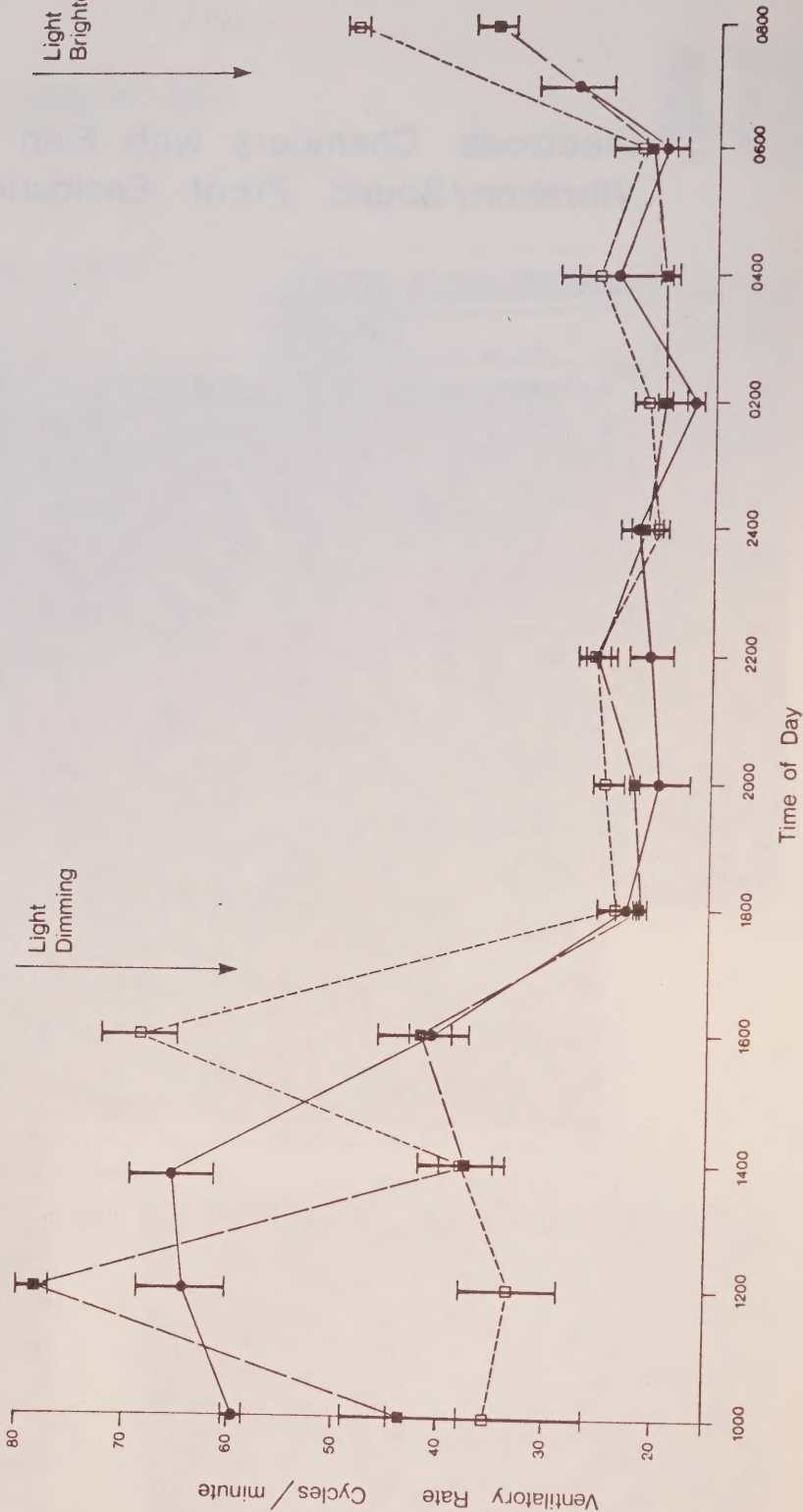


- | | |
|---------------------|-----------------------|
| 1 Fish Feeding Tube | 3 Chamber Barrier |
| 2 Electrode Chamber | 4 Low Lighting Source |

Diurnal Variation in Respiratory Rate of an Acclimated Largemouth Bass

Experiment 1 Control Fish 1

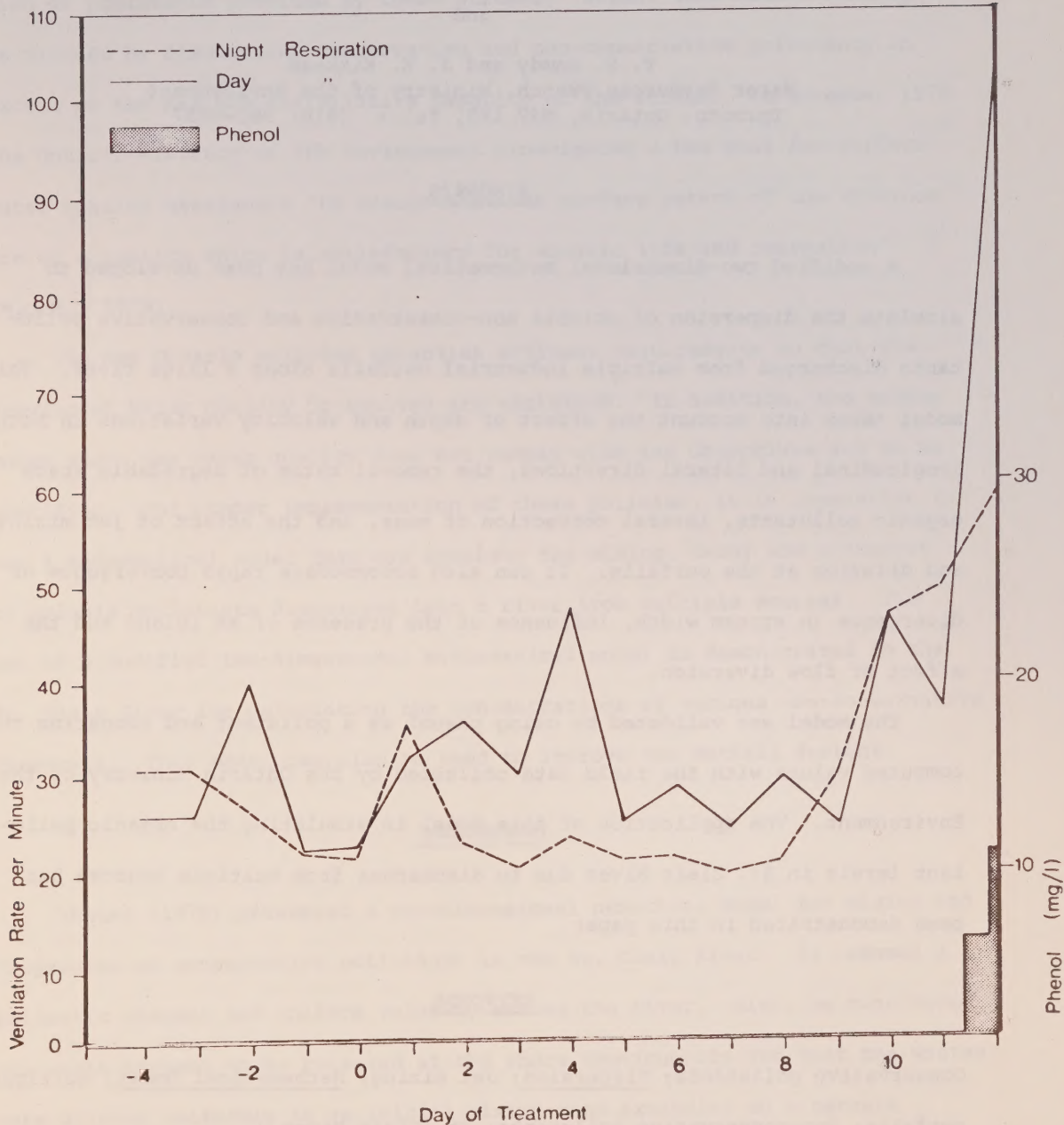
- Experimental Day 5
- " " 6
- " " 7



4.18

Ventilatory Response of Phenol Exposed Fish

Fish 8



TRANSPORT OF POLLUTANTS IN NATURAL STREAMS

by

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SYNOPSIS

A modified two-dimensional mathematical model has been developed to simulate the dispersion of soluble non-conservative and conservative pollutants discharged from multiple industrial outfalls along a large river. This model takes into account the effect of depth and velocity variations in both longitudinal and lateral directions, the removal rates of degradable trace organic pollutants, lateral convection of mass, and the effect of jet mixing and dilution at the outfalls. It can also accommodate rapid convergence or divergence in stream width, influence of the presence of an island and the effect of flow diversion.

The model was validated by using phenol as a pollutant and comparing the computed values with the field data collected by the Ontario Ministry of the Environment. The application of this model in simulating the organic pollutant levels in St. Clair River due to discharges from multiple sources has been demonstrated in this paper.

KEYWORDS

Conservative pollutants; Dispersion; Jet mixing; Mathematical model; Multiple outfalls; Non-conservative pollutants; St. Clair River.

INTRODUCTION

The disposal of domestic and industrial wastewaters into natural streams has been practiced extensively because of the dilution and natural assimilation of pollutants provided by these streams. Often, this method of disposal is misused by discharging conservative and non-conservative pollutants in excess of the maximum assimilative capacity of the stream. In November 1978 the Ontario Ministry of the Environment promulgated a new goal for surface water quality management 'to ensure that the surface waters of the Province are of a quality which is satisfactory for aquatic life and recreation' (M.O.E., 1978).

The new Ontario policies establish effluent requirements so that the Provincial Water Quality Objectives are satisfied. In addition, the mixing zones where the water quality does not comply with the Objectives are to be specified. For proper implementation of these policies, it is imperative to use a mathematical model that can simulate the mixing, decay and transport of soluble pollutants discharged into a river from multiple sources. The use of a modified two-dimensional mathematical model is demonstrated in the St. Clair River for calculating the concentrations of various non-conservative chemicals. This model can also be used to improve the outfall designs.

BACKGROUND

Akhtar (1978) presented a two-dimensional numerical model for mixing and dispersion of conservative pollutants in the St. Clair River. He assumed a prismatic channel and uniform velocity across the river. Also, he considered the waste streams to be released at the shore continuously and that the wastes were diluted uniformly in an initial mixing zone extending to a certain

distance from the shore. Most other investigators, e.g. Fischer et al. (1979) and Lau et al. (1981), have used a similar approach in calculating pollutant concentrations in the rivers. This approach was not considered adequate in simulating the dispersion of non-conservative pollutants under actual conditions with multiple outfalls in the St. Clair River. Therefore, the model was modified to include (i) the effect of depth and velocity variations in both longitudinal and lateral directions; (ii) the effect of rapid convergence or divergence of stream width; (iii) lateral convection of mass; (iv) the effect of flow diversion; (v) the effect of jet mixing and dilution at shore-based and extended outfalls; and (vi) the removal rates of degradable trace organic pollutants.

DEVELOPMENT OF MODEL

The following steps are involved in developing most numerical models:

(i) identify the domain; (ii) develop the governing equations; (iii) formulate initial conditions for the problem; (iv) formulate boundary conditions; (v) select a method to solve the governing equations; (vi) prepare a computer program; and finally (vii) test the stability and convergence of solution, calibrate the model, verify, validate and check conservation.

The present numerical model can be divided into two essential inter-related parts: river hydrodynamics model and pollutant transport model. The transport of pollutants can be treated in Eulerian coordinates, i.e., change in concentration with time at a fixed location as the flow passes by or Lagrangian coordinates, i.e., change in concentration with time as the fluid moves through space. Normally, the Eulerian method is more readily usable in practice; however, the Lagrangian method has proven useful for certain stochastic methods. The Eulerian approach is used here.

Hydrodynamic Model

The basic equations for depth averaged steady motion in a channel with variable depth are (Rodi, 1980):

$$[1] \quad \frac{\partial(hU)}{\partial x} + \frac{\partial(hV)}{\partial y} = 0$$

$$[2] \quad U \frac{\partial U}{\partial x} + V \frac{\partial U}{\partial y} = -g \frac{\partial H}{\partial x} + \frac{1}{\rho h} \frac{\partial(h \bar{\tau}_{xy})}{\partial y} - \frac{\tau_{bx}}{\rho h}$$

where x and y = longitudinal and lateral distances in Cartesian coordinates; U and V = depth averaged velocity components in x and y directions; ρ = fluid density; g = acceleration due to gravity; $\bar{\tau}_{xy}$ = average shear intensity in the vertical plane acting in the longitudinal direction; τ_{bx} = shear intensity along bed in longitudinal direction; $H = h + h_z$; h = flow depth and h_z = bed elevation. The left-hand side of momentum transport Eq. 2 represents the convective terms, whereas the right-hand side is made up of gravity, lateral shear and bed shear, respectively.

For turbulent motion, the following two equations have been proposed (Rodi, 1980):

$$[3] \quad \frac{\partial(Uk)}{\partial x} + \frac{\partial(Vk)}{\partial y} = \frac{\partial}{\partial x} (\epsilon_m \frac{\partial k}{\partial x}) + \frac{\partial}{\partial y} (\epsilon_m \frac{\partial k}{\partial y}) + G + P_{kv} - \epsilon$$

$$[4] \quad \frac{\partial(U\epsilon)}{\partial x} + \frac{\partial(V\epsilon)}{\partial y} = \frac{\partial}{\partial x} (\epsilon_m \frac{\partial \epsilon}{\partial x}) + \frac{\partial}{\partial y} (\epsilon_m \frac{\partial \epsilon}{\partial y}) + C_1 \frac{\epsilon}{k} G + P_{\epsilon v} - C_2 \frac{\epsilon^2}{k}$$

where k = turbulent kinetic energy; ϵ = turbulent diffusion coefficient; ϵ_m = eddy viscosity; G = production of k due to horizontal velocity gradients; P_{kv} = effective production of k due to non-uniform vertical gradients; $P_{\epsilon v}$ = effective production of ϵ due to non-uniform vertical gradients; and C_1, C_2 = constants. The left-hand side of Eq. 4 represents convection terms, whereas on the right-hand side, the first two terms represent dispersion, the next two terms generation and the last term dissipation. Certain variables

in the mean and turbulent motion equations are interrelated as given below:

$$[5] \quad \varepsilon_m = C_\mu \frac{k^2}{\varepsilon}$$

$$[6] \quad \bar{\tau}_{xy} = \rho \varepsilon_m \left(\frac{\partial U}{\partial y} + \frac{\partial V}{\partial x} \right) - \frac{2}{3} k$$

$$[7] \quad \tau_{bx} \cong C_f \rho U^2$$

where ρ is fluid density and C_μ , C_f are coefficients.

In order to avoid the computational complexity and cost associated with solving the turbulence transport model, a simplified hydrodynamic model was introduced in which it is assumed that the lateral depth profiles and river flow rates are available and can be used to obtain velocity profiles at different sections along the longitudinal direction. Using the Manning's equation to account for the effect of vertical momentum transfer and a shape function to account for side effects, the local vertically averaged longitudinal velocity, $U(y)$, in a grid of a wide channel with constant slope, S_e , is given by:

$$[8] \quad U(y) = \chi(y) \frac{h^{2/3} S_e^{1/2}}{n}$$

where n = Manning's roughness factor; h = average depth in a specified grid point; and $\chi(y)$ = shape factor accounting for the bank effects.

In Eq. 8, $U(y) = 0$ when $y = 0$ and again when $y = w$ = channel width.

The proposed equation for shape factor is:

$$[9] \quad \chi(y) = \left[-\left(\frac{y}{w} - \frac{1}{2} \right)^2 + \frac{1}{4} \right]^{n_1}$$

where n_1 = empirical exponent; and y = lateral distance of section from shore.

The values for n , n_1 and S_e are chosen to best fit the available data. In addition, the continuity equation (Eq. 1) should also be satisfied, i.e.,

$$[10] \quad Q = \int_0^W U(y) h \, dy$$

The depth averaged velocity in the lateral direction, $V(y)$, can be computed by integration of Eq. 1, i.e.,

$$[11] \quad V(y) = -\frac{1}{h} \int_0^y \frac{\partial(hU)}{\partial x} \, dy$$

Pollutant Transport Model

Using the Eulerian approach, the rate of change in pollutant concentration, C , during transport under turbulent conditions is given by

$$[12] \quad \frac{\partial C}{\partial t} = -\left\{ \frac{\partial(UC)}{\partial x} + \frac{\partial(VC)}{\partial y} + \frac{\partial(WC)}{\partial z} \right\} + \left\{ \frac{\partial(-\overline{u'c'})}{\partial x} + \frac{\partial(-\overline{v'c'})}{\partial y} + \frac{\partial(-\overline{w'c'})}{\partial z} \right\} \\ + P_r - D_e$$

where z = vertical distance; W = ensemble averaged velocity component in z direction; u' , v' , w' and c' = deviation from depth average value of U , V , W and C , respectively; P_r = production rate; and D_e = decay rate. Overbars imply temporal averages. The first three terms on the right-hand side of Eq. 12 represent the net mass movement by convection and the next three terms represent the turbulent exchange.

The pollutant concentrations at different stream sections are computed by considering dilution, dispersion and degradation of pollutants in the following steps:

- I. Dilution due to initial mixing of pollutants discharged from different outfalls into the stream (near field);
- II. Further dilution of pollutants due to dispersion during transport in the stream (far field); and
- III. degradation of pollutants during transport in the stream.

I. The near field mixing of pollution from an idealized source and domain is computed analytically. The concept of initial mixing without

buoyancy has been reported by Camp and Meserve (1974) and Rajaratnam (1976). Rajaratnam has also described the mixing characteristics and trajectories of cross jets. For example, the trajectory of the centreline of a jet can be approximated by:

$$[13] \quad y_{inj} = 2.05 \left(\frac{V_j d_e}{U} \right)^{0.72} (x_{inj})^{0.28} \cos \theta_o$$

where y_{inj} = lateral injection distance; x_{inj} = corresponding longitudinal distance; U = local stream velocity; V_j = initial outfall velocity; d_e = equivalent outfall diameter; and θ_o = initial angle between the stream and outfall trajectory, $\leq 90^\circ$.

According to Rajaratnam, the length of potential core, ξ_o , varies from $2d_e$ to about $6d_e$ for an outfall that is submerged between the water surface and the channel bed. This core may extend up to $12d_e$ for surface or bottom outfalls with low relative outfall velocities. The dilution ratios, S , for a circular and a rectangular outfall are given respectively by:

$$[14] \quad S = 1 + 0.32 \left(\frac{\xi}{d_e} \right)$$

$$[15] \quad S = \left[1 + 0.07 \frac{\xi}{w_o} \right] \left[1 + 0.035 \frac{\xi}{d_o} \right]$$

where ξ is the trajectory distance from the outfall; w_o = width of outfall; and d_o = depth of outfall. The area of the sub-section to be used for the initial mixing is approximately $(S \times \text{outfall area} \times \alpha_j)$ where $\alpha_j = V_j/U(y)$. A distance y_{proj} must be added to y_{inj} to determine the lateral position of the mixing sub-section for extended outfalls, Fig. 1. It is assumed that the shore-based outfalls will create a small wake zone extending approximately $3y_{inj}$ downstream from the outfall. Concentrations in this zone are assumed to be more dependent on those in the outfall than on the pre-existing stream concentrations.

The near field and far fields are represented and discretized as shown in Fig. 1. A special initial condition is required at each outfall. The pollutant is mixed into a preselected stream sub-section, shown shaded in Fig. 1, by applying the mass balance equation. The location and dimensions of this sub-section depend on the outfall characteristics, such as its size, shape, exit velocity, projection into the stream, position relative to the water surface, inclination to the shore and densimetric Froude number. The pollutant concentration in this sub-section, $C(I,J)$, is obtained from:

$$[16] \quad C(I,J) = \frac{C'(I,J)Q'(I,J) + C_o(I_f)[Q_o(I_f)/a_{jet}]\Delta y}{Q'(I,J) + Q'(I_f)}$$

where $C'(I,J)$ = concentration at (I,J) without the outfall contribution;
 $Q'(I,J)$ = river flow through the area of influence of (I,J) excluding the outfall discharge; $C_o(I_f)$ = pollutant concentration at outfall I_f ; $Q_o(I_f)$ = discharge of outfall I_f ; and a_{jet} = width of near field jet at the beginning of far field.

II. The general transport Eq. 12 is simplified to the following two-dimensional convection-dispersion equation for concentration, C , of a non-conservative pollutant in a natural stream by assuming depth-averaged steady state conditions:

$$[17] \quad \frac{\partial U h C}{\partial x} + \frac{\partial V h C}{\partial y} = \frac{\partial}{\partial x} [h(-\overline{u'c'})] + \frac{\partial}{\partial y} [h(-\overline{v'c'})] + h P_r - h D_e$$

The differential longitudinal advection, $\overline{u'c'}$, and the differential lateral advection, $\overline{v'c'}$, are related to the longitudinal dispersion coefficient, ϵ_x , and lateral dispersion coefficient, ϵ_y , respectively, by the following equations:

$$[18] \quad \overline{u'c'} = -\epsilon_x \frac{\partial C}{\partial x}$$

$$[19] \quad \overline{v'c'} = -\epsilon_y \frac{\partial C}{\partial y}$$

The following further assumptions are made for flows in rivers: (i) the longitudinal dispersion term is relatively small as compared to the longitudinal convection term and is neglected; and (ii) the contributions from the multiple outfalls are introduced at appropriate points and P_r is assumed to be zero. Consequently, Eq. 17 is reduced to the following form:

$$[20] \quad \frac{\partial U h C}{\partial x} + \frac{\partial V h C}{\partial y} = \frac{\partial}{\partial y} (h \epsilon_y \frac{\partial C}{\partial y}) - h D_e$$

In this equation, the dispersion coefficient is assumed to be proportional to the shear velocity, U_* , and the depth of flow (Hamdy and Kinkead, 1979)

$$[21] \quad \epsilon_y = \alpha U_* h$$

where α is a dispersion factor and the shear velocity is obtained from:

$$[22] \quad U_* \approx nu\sqrt{g}/h^{1/6}$$

where u is the local river velocity, n is Manning's n and h is the local depth.

III. Bobra and MacKay (1980), Snodgrass (1980) and others have proposed the following equations for decay of pollutants after mixing in the stream. The important parameters influencing the decay are volatilization (evaporation), biodegradation, free radical oxidation, hydrolysis and photolysis.

$$[23] \quad D_e = [k_{EV} + k_{BD} + k_{OX} + k_{HY} + k_{PH}]_{20} C \theta^{(T-20)} \\ = k_{20} C \theta^{(T-20)}$$

where k_{EV} = rate constant for evaporation; k_{BD} = rate constant for biodegradation; k_{OX} = rate constant for free radical oxidation; k_{HY} = rate constant for hydrolysis; k_{PH} = rate constant for photolysis; k_{20} = overall decay rate constant; T = temperature, °C; and θ = Arrhenius constant. Since evaporation

rate constant, k_{EV} , is inversely proportional to the depth of flow, h , (Bobra and MacKay, 1980) Eq. 23 was modified to include the effect of varying depth of flow in the stream by replacing k_{EV} with K_{OL}/h where K_{OL} is mass transfer rate for evaporation in ms^{-1} .

Bobra and MacKay (1980) and Snodgrass (1980) conducted literature surveys to obtain information on the degradation of various pollutants, both in natural bodies of water and under controlled laboratory conditions and have suggested appropriate values for rate constants.

DESCRIPTION OF FAR FIELD NUMERICAL MODEL

For far field transport of pollutants, finite difference methods were used to solve Eq. 20. The channel is discretized by using a rectangular grid in the x (longitudinal) and y (lateral) directions as shown in Fig. 1. The grid size must be specified such that:

$$DX = DSTN/N$$

$$DY = DDY/M$$

where $DSTN$ = distance between input cross-sections; N = integer; DDY = width increment between input depths in each cross-section; M = integer.

For channels with small lateral convection, e.g., nearly prismatic channels with no diversions or confluences, $DX \leq 2.5 DY$. If large lateral convection occurs, numerical instabilities may result, and DX may have to be reduced, but $DX \geq DY$.

Equation 20 can be treated as having three separate components, i.e. convection along the streamlines, dispersion normal to the streamlines and decay. Convection and dispersion are conservative processes while the decay term accounts for loss of mass. Since the uncoupled transport equation is linear, the conservative and non-conservative terms can be separated in the

differencing scheme. In this way, errors due to fictitious or numerical decay can be detected and adjustments made to the solution. Since the transport process in the far field is assumed to be unaffected by recirculation, a forward marching scheme can be used. Therefore, it is possible to discretize the domain as shown in Fig. 1.

Two approaches were used in treating the convective term: (a) forward finite difference scheme in the x-y plane and (b) a stream function approach in which the transportation along the streamlines is used. Method (a) was used for low lateral convection, while method (b) was used for high lateral convection. The lateral velocity, V , was obtained from Eq. 11 by

$$[24] \quad V(I + \frac{1}{2}, J) = \left\{ \sum_{1}^J U(I, J + \frac{1}{2}) [h(I, J + \frac{1}{2})] - \sum_{1}^J U(I+1, J + \frac{1}{2}) [h(I+1, J + \frac{1}{2})] \right\} \Delta y / [\Delta x h(I + \frac{1}{2}, J)]$$

while U was obtained from Eq. 8 as

$$[25] \quad U(I, J) = \chi[Y(I, J)] [h(I, J)]^{2/3} K(I)$$

where $K(I) = Q / \left\{ \sum_{J=1}^N \chi[Y(I, J + \frac{1}{2})] [h(I, J + \frac{1}{2})]^{2/3} \Delta y \right\}$; N = number of increments of width Δy across the channel.

The convective term in x-direction is represented at $(I + \frac{1}{2}, J)$ by a forward difference, i.e.

$$[26] \quad \frac{\partial (hUC)}{\partial x} \approx \frac{1}{\Delta x} \{ h(I+1, J) U(I+1, J) C(I+1, J) - h(I, J) U(I, J) C(I, J) \}$$

A general differencing scheme at $(I + \frac{1}{2}, J + \beta - \frac{1}{2})$ is used to approximate the lateral convection, thus

$$\begin{aligned}
 [27] \quad \frac{\partial(hVC)}{\partial y} \approx & C(I, J+1) \left[\frac{1}{2} (1-\beta) \frac{Q_v}{\Delta y} \right] + C(I, J) \left[\frac{1}{2} (2\beta-1) \frac{Q_v}{\Delta y} + \frac{1}{2} \frac{\Delta Q(J)}{\Delta x} \right] \\
 & + C(I, J-1) \left[-\frac{1}{2} \beta \frac{Q_v}{\Delta y} \right] + C(I+1, J+1) \left[\frac{1}{2} (1-\beta) \frac{Q_v}{\Delta y} \right] \\
 & + C(I+1, J) \left[\frac{1}{2} (2\beta-1) \frac{Q_v}{\Delta y} + \frac{1}{2} \frac{\Delta Q(J)}{\Delta x} \right] + C(I+1, J-1) \left[-\frac{1}{2} \beta \frac{Q_v}{\Delta y} \right]
 \end{aligned}$$

in which $\Delta Q(J) = [U(I, J)h(I, J) - U(I+1, J)h(I+1, J)]$; $Q_v = \frac{\Delta y}{\Delta x} \sum_{J=1}^J \Delta Q(J)$;

β = a parameter such that $\beta = 0$ gives backward difference, $\beta = \frac{1}{2}$ central difference and $\beta = 1$ forward difference in the y-direction. The parameter can be used to introduce upwinding in the lateral direction.

The lateral dispersion term is differenced at $(I + \frac{1}{2}, J)$, i.e. using central differences to yield

$$\begin{aligned}
 [28] \quad \frac{\partial}{\partial y} (h \epsilon_y \frac{\partial C}{\partial y}) \approx & C(I, J+1) \left\{ \frac{1}{4} [h(I, J+1) \epsilon(I, J+1) + h(I, J) \epsilon(I, J)] \right\} / \Delta y^2 \\
 & + C(I, J) \left\{ -\frac{1}{4} [h(I, J+1) \epsilon(I, J+1) + h(I, J) \epsilon(I, J)] \right. \\
 & \left. + h(I, J) \epsilon(I, J) + h(I, J-1) \epsilon(I, J-1) \right\} / \Delta y^2 \\
 & + C(I, J-1) \left\{ \frac{1}{4} [h(I, J) \epsilon(I, J) + h(I, J-1) \epsilon(I, J-1)] \right\} / \Delta y^2 \\
 & + C(I+1, J+1) \left\{ \frac{1}{4} [h(I+1, J+1) \epsilon(I+1, J+1) \right. \\
 & \left. + h(I+1, J) \epsilon(I+1, J)] \right\} / \Delta y^2 \\
 & + C(I+1, J) \left\{ -\frac{1}{4} [h(I+1, J+1) \epsilon(I+1, J+1) + h(I+1, J) \epsilon(I+1, J)] \right. \\
 & \left. + h(I+1, J) \epsilon(I+1, J) + h(I+1, J-1) \epsilon(I+1, J-1) \right\} / \Delta y^2 \\
 & + C(I+1, J-1) \left\{ \frac{1}{4} [h(I+1, J) \epsilon(I+1, J)] \right. \\
 & \left. + h(I+1, J-1) \epsilon(I+1, J-1) \right\} / \Delta y^2
 \end{aligned}$$

Equations 26, 27 and 28 may be combined to form a tridiagonal matrix in the unknown values of C at I+1 and a vector composed of the boundary conditions at section I.

This system may be solved by a Crank-Nicholson approach using forward elimination and backward substitution (Smith, 1965). By evaluating the mass flux, $\int_0^w U_h C dy$, at I and at I+1 before the decay has been included, artificial or numerical decay can be detected. Before proceeding, the computed values of C at I+1 based on convection and dispersion are increased or decreased to account for any artificial loss or gain in mass flux.

The C values at I+1 are then corrected for real decay. This correction is based on the transit time from I to I+1 (x to $x+\Delta x$) and is given by

$$[29] \quad C(I+1, J) = C(I+1, 1) e^{-k_{20} \theta^{(T-20)} \Delta t}$$

where $\Delta t \approx 2\Delta x / [U(I+1, J) + U(I, J)]$

Method (b) is not given in detail here since it is similar in concept to that used by Lau (1981) except that decay is separated as in method (a).

Method (a) gave better results for reaches with low lateral convection, whereas Method (b) is preferred where lateral convection is large. For example, if the $|(change\ in\ channel\ width)/(reach\ length)| > 0.25$, Method (b) is used by the programme.

The boundary conditions at the banks were treated as reflecting surfaces, i.e.

$$[30] \quad \frac{\partial C}{\partial y} = 0.$$

e.g. the simplest finite difference form is

$$[31] \quad C(I, 1) = C(I, 2)$$

and

$$[32] \quad C(I, N) = C(I, N-1)$$

where N = the J node at the far bank.

A new boundary or initial condition must be established at the end of the near field of each outfall. This is accomplished by Eq. 16. The equivalent jet width is estimated based on the local flow depth h and the near field dilution ratio, S , (e.g. Eq. 14 or 15),

$$[33] \quad a_{\text{jet}} \approx \left\{ \frac{S Q_o(I_f)}{h(y)U(y)} \right\} y_{\text{inj}} + y_{\text{proj}}$$

If the outfall flow, $Q_o(I_f)$, is large compared to the river flow into which it is being mixed, $Q(I_f)$ must be dispersed in the far field. In other words, if S is small, the outfall flow must be dispersed along with the pollutant.

The flow chart for the computer programme is shown in Fig. 2.

CASE STUDY FOR QUALITY OF SOLUTION

The quality of solution obtained by numerical analysis should be tested for accuracy, numerical dispersion, boundedness error, computational stability, convergence (truncation and iteration) and conservation. In order to test the quality of solution, this numerical model was applied to a 12 km stretch of the St. Clair River, shown in Fig. 3, to obtain lateral and longitudinal concentration profiles of non-conservative compounds under given loading rates and streamflow conditions. In all, effluent discharges from twenty-four sources at nineteen different locations, as shown in Fig. 3, were considered in the simulations. Each of these outfalls had different characteristics and loading rates. Five chemicals--phenol, benzene, toluene, methylene chloride and carbon tetrachloride--were analyzed. The decay rate constant values were

taken from the unpublished report prepared by Bobra and MacKay (1980). The following assumptions were made in the simulation runs:

River flow rate (mean) = $5240 \text{ m}^3/\text{s}$

Water temperature = 20°C

Arrhenius constant = 1.06

The rate constant values in (s^{-1}) for phenol are: $K_{EV} = .01 \times 10^{-5}$; $K_{BD} = 0.17 \times 10^{-5}$; $K_{OX} = 0.17 \times 10^{-5}$; $K_{HY} = 0$; $K_{PH} = 1.65 \times 10^{-5}$.

Actual lateral depth profiles for mean river flow at every 300 m longitudinal distance and 15 m lateral distance were used. These data were obtained from surveys by the Ontario Ministry of the Environment and from the U.S. Department of Commerce Maps No. 46-49/14853 (Nautical Chart Catalogue No. 4, Panel C). Manning's Coefficient, $n = 0.0235$, as suggested by the U.S. Corps of Engineers, was used to generate hydraulic data for flows and velocities. The non-dimensional dispersion coefficient of 0.96 was observed by Hamdy and Kinkead (1979) for the St. Clair River and was used in these calculations. At a longitudinal distance of 7900 m, the river flow splits in two parts around Stag Island. It is estimated that the flow in the channel along the Canadian shore is approximately one-third of the total flow.

Figure 3 shows the result obtained for phenol with zero background values. The contours for C are in $\mu\text{g/L}$. Similar data were obtained for other pollutants and are reported elsewhere (McCorquodale et al., 1980). The contours indicate the extent of mixing zones for pollutants in different concentrations. It is observed that the spreads of these mixing zones are influenced by the changes in depth and velocity profiles both in lateral and longitudinal directions. As the water moves laterally away from the shore due to decrease in water depth, the contour lines also drift away from the shore. Similarly, due to increase in depth of flow near the shore, the

contour lines move towards the shore. It is also observed that the pollutants disperse slowly when discharged in a shallow, slow-moving zone of the river, but once these pollutants reach the deeper and fast-moving zone of the river, the dispersion of these pollutants becomes very rapid.

Figure 3 shows a very distinct influence of outfall characteristics. The pollutant concentration after initial mixing depends both on the type of outfall and the quantity of wastewater added. The deeper the zone of initial mixing, the faster the lateral dispersion of pollutants into the river. This is particularly true with multi-port extended outfalls. It is obvious that a proper design and location of outfall is a very important factor in the dispersion of pollutants in the receiving stream, and this numerical model can help in selecting the best design.

The results obtained for phenol with this numerical model are compared in Fig. 4 with the field data collected by the Ontario Ministry of the Environment. There is a reasonable agreement in the computed and observed concentration values.

CONCLUSIONS

The numerical model presented in this paper is capable of predicting the concentrations of non-conservative and conservative pollutants discharged from multiple outfalls into a river. It can also be used in identifying the mixing zone, designing the type and location of outfalls, and computing the maximum allowable wastewater load from different outfalls in order to control the level of any pollutant in the river.

ACKNOWLEDGEMENT

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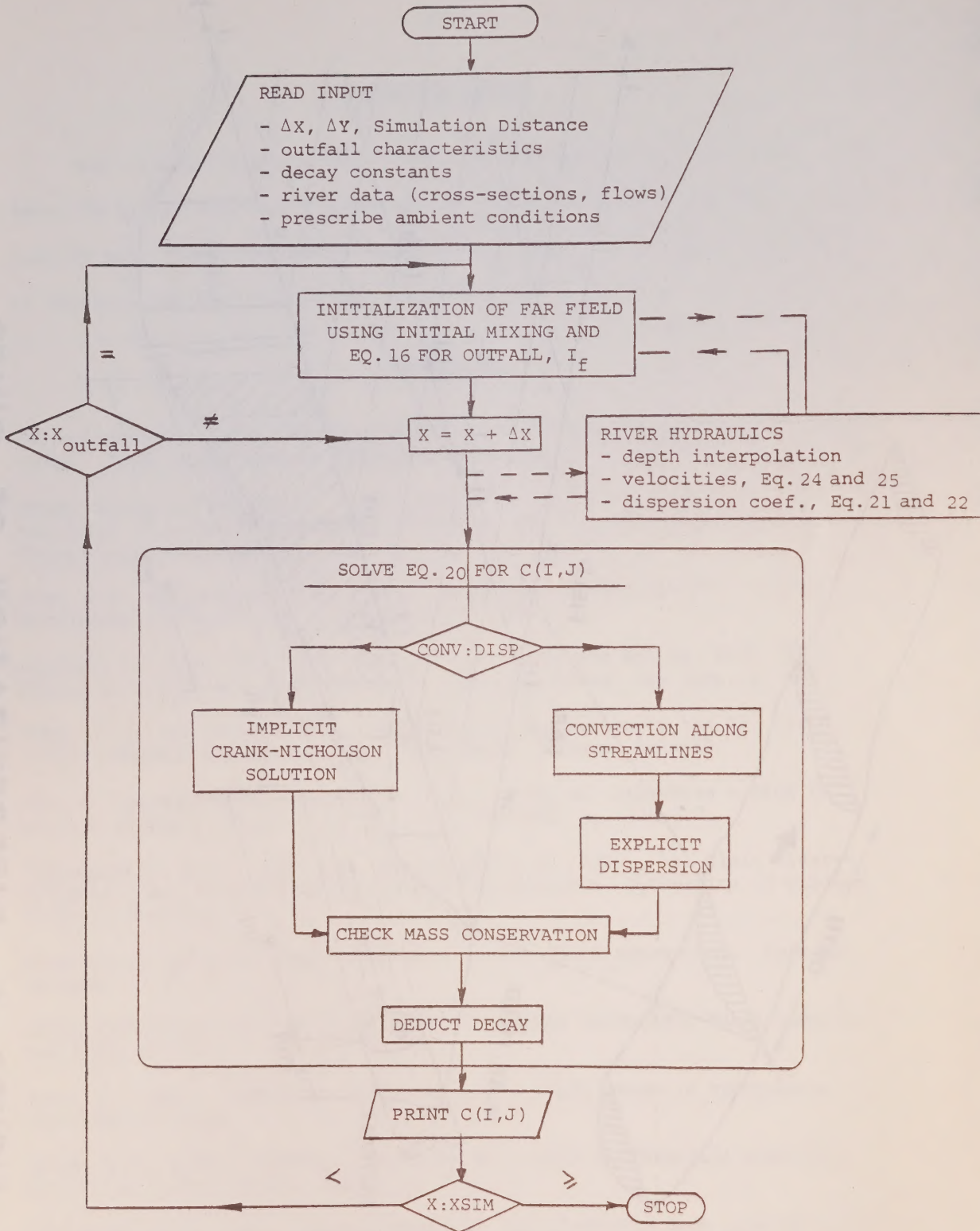


FIG. 2 Flow Chart of Mathematical Model

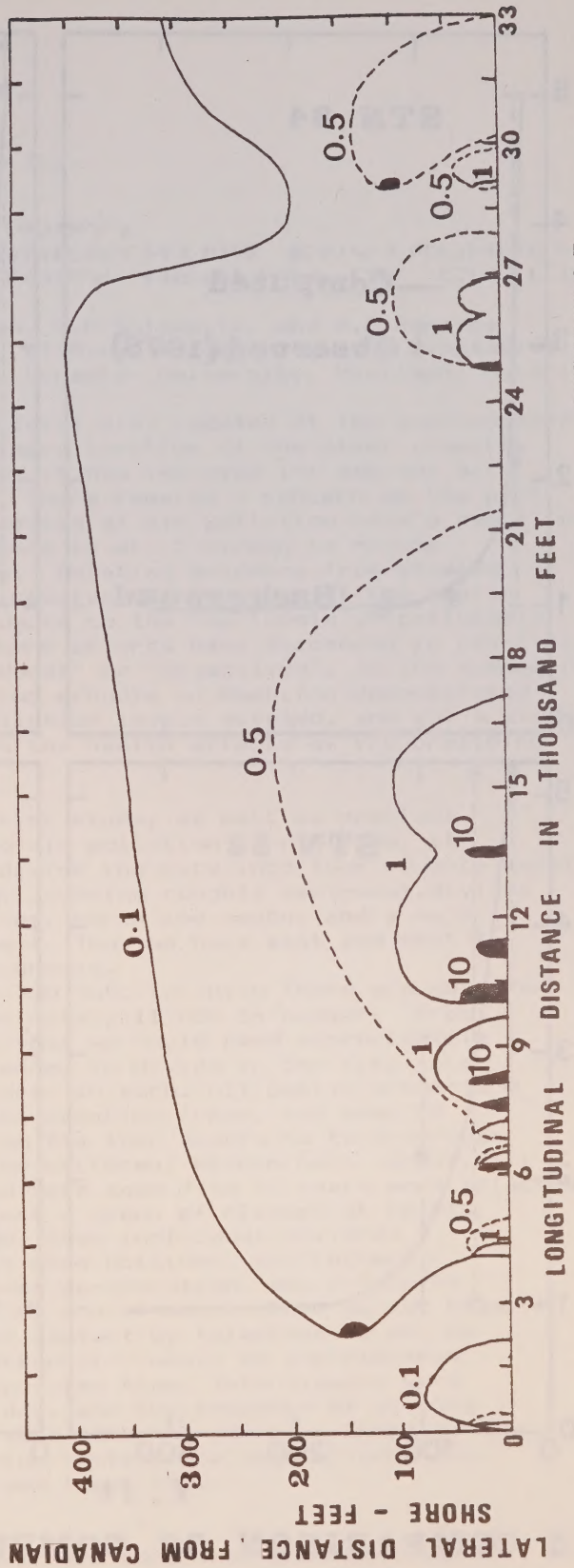
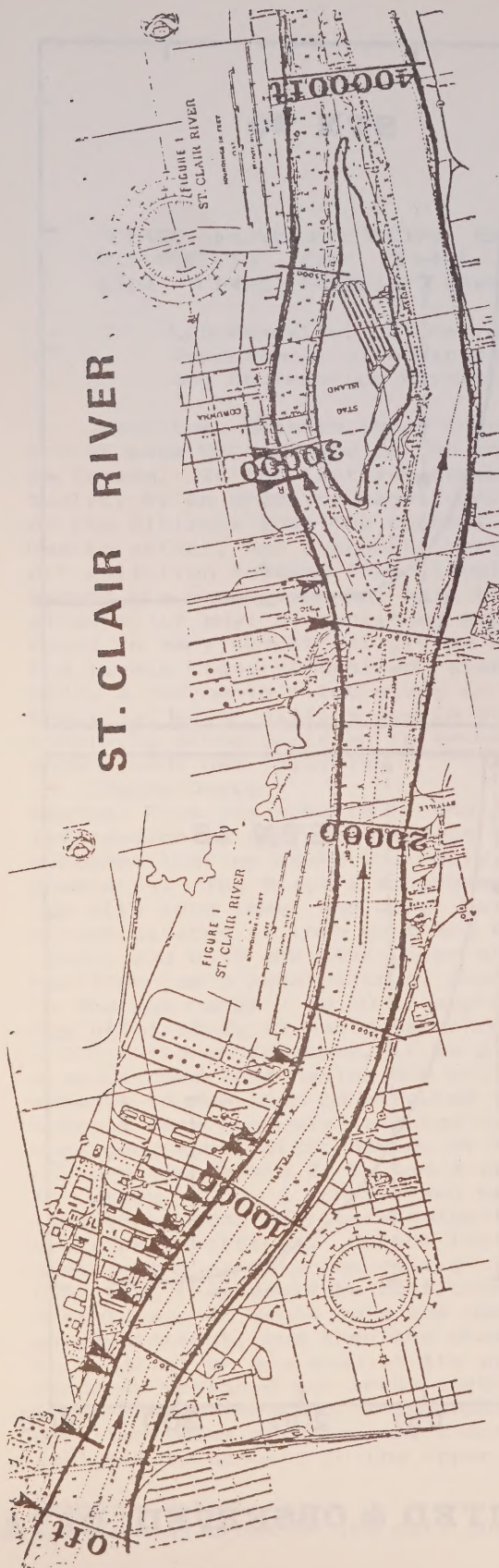


FIGURE 3 - POLLUTANT CONCENTRATION CONTOURS - PHENOL - $\mu\text{g/L}$

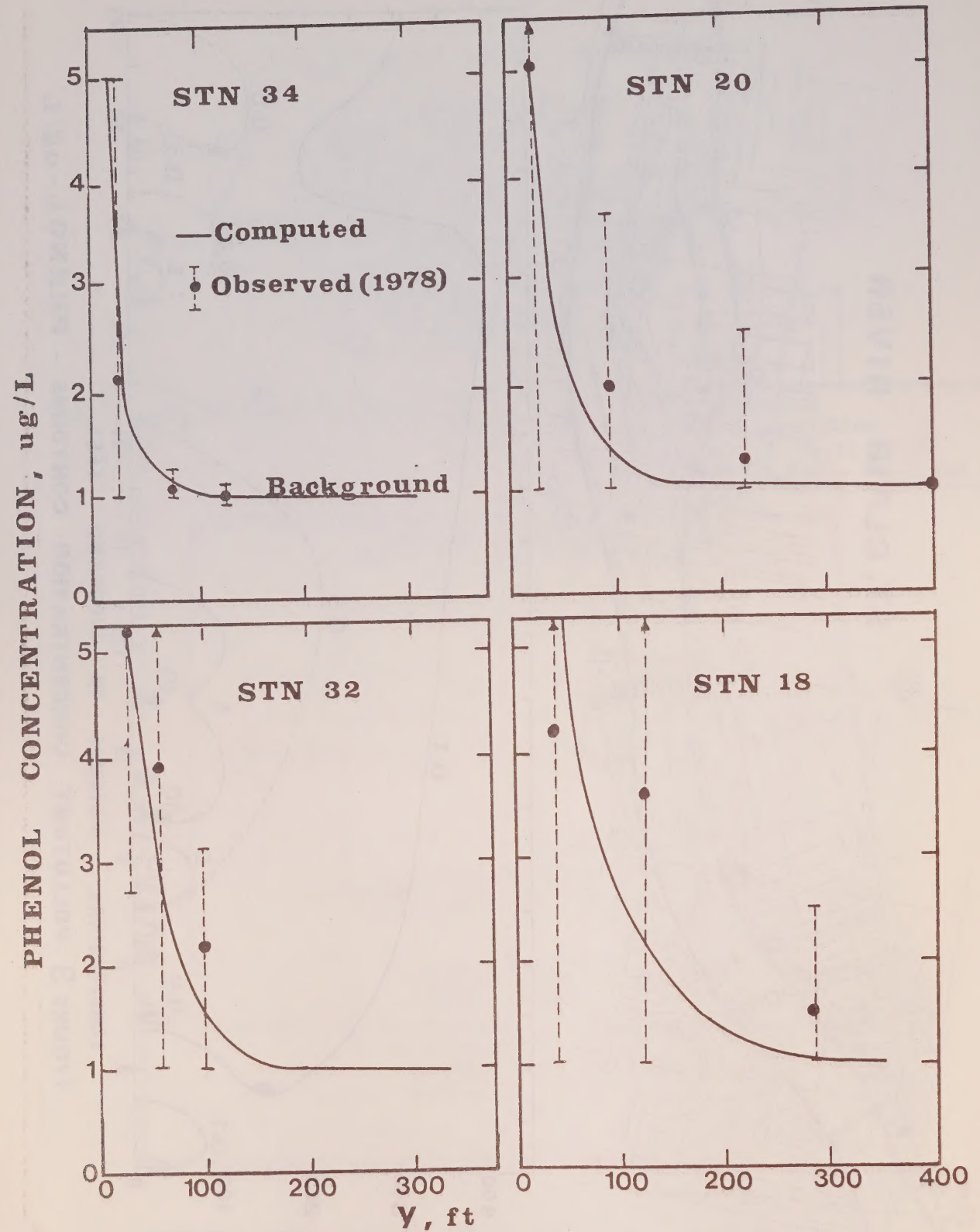


FIG4 COMPARISON OF COMPUTED & OBSERVED DATA

THE HAMILTON STUDY: EFFECT OF THE BREATHING ENVIRONMENT ON THE RESPIRATORY HEALTH OF CHILDREN

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Hamilton, Ontario is an industrial city located at the southwestern end of Lake Ontario and is the primary location of the steel industry in Canada. In the last two decades it has improved its ambient air quality by an order of magnitude. There remains a concern on the part of its citizens that the current levels of air pollution have a negative health effect, and community pressure is still strong to reduce air pollution to even lower levels. Existing evidence from studies around the world does not help to resolve the question of the health effects (if any) of continued exposure to the low levels of pollutants found in many industrial cities where efforts have succeeded in reducing the levels close to desired "standards" or "objectives". In the summer of 1977, a two-month pilot study in two schools in Hamilton demonstrated that: (a) major differences in pollution levels existed, and (b) a study involving schoolchildren to assess the health effects of the breathing environment was feasible.

Study Design

Sample. From the results of the pilot study, as well as previous information we had with respect to air pollution in Hamilton, it appeared that we could logically divide the city into four roughly equal quadrants. The Niagara escarpment, running roughly east-west, divides the city into lower and upper halves, north and south; and a major street divides it into east and west. Thus we have east and west lower, and east and west upper quadrants. Hamilton has a population of over 300 000, in which there are children in the age range 7 to 10 yr approximately 11 000 in number. From the pilot study it was determined that we would need approximately 3 200 children to study, if we planned to divide up the city into 4 equal quadrants having 800 children in each. All public elementary schools in Hamilton constituted the sampling frame, and some 30 schools were randomly selected from the four quadrants to ensure an even geographic distribution of the children. Within each school, all children in levels 2, 3, and 4 who were aged 7 to 10 years were selected for study. Once a school, and hence a group of classes at levels two, three, and four were selected, then individual children could be identified. School lists were obtained, and letters sent to the parents requesting their co-operation, and informing them that they would be contacted by one of our trained survey team. A field worker would make the next contact by telephone to set up an appointment, and then the questionnaire would be administered to a parent or guardian at the appointed time. Interviewers were randomly assigned new areas each day, and the sequence of schools to be interviewed and tested was also taken at random. There were two teams of pulmonary function testers who were alternately assigned to schools in the upper and lower city.

Response Rates.

For each quadrant of the city there were more than the required

number of interviews completed in Year 1, and again in Year 2, the response rate being in excess of 95% of those eligible in both years. Over 85% of the children tested in Year 1 were retested in Year 2, and this rate is holding steady for that part of Year 3 already completed. For any survey these are unusually high figures, and we are most grateful to our skilled teams of interviewers and testers for their excellent work.

Interviews. The interviewers inquire about the child's respiratory health by asking questions about cough, wheezing, days off school because of respiratory illness, and frequency and type of colds. In addition, aspects of the home environment such as housing, smoking in the home, cooking fuel, residential history and socio economic factors were explored via the questionnaire. At the end of the interview (which took 15 minutes), consent for the child to participate in the pulmonary function test was requested.

Pulmonary Function Testing.

Pulmonary function was measured on the children in the schools by two pulmonary function teams, each using a Hewlett-Packard 47804A pulmonary calculator system. Each system was mounted in a heavy steel console desk, and equipped with isolating transformers for an added measure of electrical safety. Each system has by now been moved over 150 times, and for the most part has performed well under difficult conditions. The teams produce reports consisting of age, weight, height, sex, race, FVC, FEV1, MMEF, FRC, CV, CC and other indices of pulmonary function. In excess of 20 indices are measured or computed. Local environmental conditions (temperature, humidity, pressure and time) are also recorded.

Quality Control.

Interviews. A random sample of 5% of all the respondents were telephoned and questions taken at random were re-asked. In all cases the interview was found to have been done, but in some 11% of the cases there was a difference between the response to the question the first and the second time. Most of these errors were resolved or considered not to be a problem. Some were likely real changes in the health status of the child, since a different time period was being asked about. No significant differences were found to be attributable to interviewers.

Pulmonary Function.

Eight children from each school (selected randomly) were re-tested. The reproducibility of most of the tests was found to be acceptable, and in those tests where a slight change was observed, it could be attributed to a "practice effect". The results of one team could also be compared with the other, and over each year testing period no systematic differences were found between teams.

All data were coded, keypunched and verified before being stored on computer file. Five % of all data taken at random were recoded by an alternate coder, and for pulmonary function tests the error rate was between 1 and 2%, while for the questionnaire the error rate was less than 0.5%. Range checks were run on all data at data storage time, yielding rates up to 3.6%, most of which were

easily resolved. Quality control procedures such as these have not previously been described for epidemiological studies of air pollution.

EXPOSURE ESTIMATION.

Particulate monitoring. TSP and PSD samplers were evenly distributed throughout Hamilton in the four quadrants in an attempt to establish the nature of the particulate size and loading gradients throughout the populated areas of the city. The TSP monitors are standard Hi-Vol samplers, using glass fibre filters, and operating at 40 cubic feet per minute (cfm) for 24 hr. on a 6-day cycle. Particulate Size Distribution (PSD) was obtained from Andersen cascade impactors operated at a flow of 20 cfm, on the same six day cycle. Filters are carefully weighed before and after exposure in a humidity and temperature controlled environment on a standardized balance, and the weights are used to estimate TSP and PSD with standard procedures in micrograms per cubic meter.

SO₂ is measured at 16 sites distributed evenly throughout the four quadrants. For six weeks of each season, instruments were placed in eight of the sites, followed by a further six weeks in the second group of eight sites. Beckman SO₂ analyzers are rotated through the sites and are checked every three days. A tunable diode laser system has been constructed and calibrated to measure SO₂ in parts per billion (ppb) concentrations. This portable laser system and a similar laboratory device are used to keep a constant calibration check on the Beckman instruments. Hourly readings of SO₂ are available from the eight sites, but mean values over days, months or seasons have been used so far in preliminary analyses.

The intensive "population-oriented" network has been in operation for 2 yr, and sufficient data have been gathered to be able to describe the nature and extent of the spatial distribution of pollution concentration throughout the city, both for TSP and for SO₂. Using standard regression techniques, a three-dimensional surface has been fitted to data obtained (for TSP) from 29 stations distributed across the city, and (for SO₂) from 18 locations across the city. Figure I shows such a surface fitted to TSP data which represent the yearly average obtained from July 1979 to June 1980. The equation which describes this surface is:

$$TSP(\mu g/m^3) = B_0 + B_1X_1 + B_{11}X_1^2 + B_2X_2 + B_{22}X_2^2 + B_{12}X_1X_2 + e,$$
where X_1 is the spatial coordinate in a "northing" direction, X_2 is the spatial coordinate in an "easting" direction, the B 's represent coefficients, and e represents a residual, or error term. X_1 and X_2 represent a square approximately 15 km on a side. Since there are six coefficients, at least 7 data points are required in order to estimate the size of the residual; 22 points were used in this example. The coefficient of variation for the surface shown in Fig. I is 61%, indicating that 61% of the variation in TSP during the year can be explained by a quadratic model in location. Even if only one month's data are used, coefficients of variation ranged from 52% to 83% for data given in this example. If meteorological factors were included, it is likely that the predictive ability of the model would be enhanced. A similar analysis has been done for the SO₂ data, as shown in Fig. II; SO₂ concentrations are expressed in ppb, and are yearly averages over

the same period.

From the surface shown in Fig. I, it is clear that a significant gradient in TSP exists over the city, from a high value of $110 \mu\text{g}/\text{m}^3$ to a low of approximately $30 \mu\text{g}/\text{m}^3$ found in the suburban and rural areas. The shape of the surface for SO_2 shown in Fig. II is quite different to that found for TSP, and indicates the presence of two areas of high concentration, rather than the single one shown for TSP. From these examples, it can be seen that an assumption of uniform air pollution concentration in space cannot be supported in an urban area, and that the shape of the distribution depends on the nature of the pollutant and the location of its sources. Using the method of response surface estimation described here, we are able to predict with some confidence the level of pollutant to be expected at any location within the area in which we have data. Thus, we can estimate the average exposure for a month (or other time period) at the school and home locations within the city. By using these estimates of air quality at specific locations for particular time periods, exposures could be individualized to school, home and possibly even a child measured at a particular time who spent P proportion of the time at school and $(1-P)$ proportion at home.

INDOOR SAMPLING.

A modification of the Yale personal sampler has been developed for use as an indoor multipollutant sampler. Measurements of SO_2 , NO_2 and suspended particulate are made, averaging over a 24 hr. period. The sampler is quiet, unobtrusive and line-operated, and can be serviced in a few minutes. Two networks of indoor samplers; 16 schools and 24 homes have been set up, together with complementary similar outdoor samplers. The networks are designed to provide broad geographical coverage, as well as to examine the indoor-outdoor ratio of different types of structures. This information plus a detailed questionnaire related to building insulation, heating and cooling technology, windows etc. should provide us some more insight into the breathing environment of the children in the study.

In Hamilton, the indoor-outdoor samplers have been in operation a much shorter period of time, and data are only recently becoming available. An example of typical results in a school can be seen in Table I. Two indoor locations were sampled, a typical classroom, and the staff room. Note that the indoor levels for SO_2 are low, and close to the outside levels, as are the values for NO_2 . At this location, a hi-vol TSP sampler is also operated outside, as well as a hi-vol equipped with an Andersen cascade impactor producing PSD information. The level of particulates measured by the outside multipollutant sampler was close to that measured by the 2 hi-vol samplers. In the classroom, the particulate level was also close to the outside level, but in the staff room, the levels were much higher. In the school studies, it has been observed that many of the teachers smoke cigarettes during their time in the staff room, and the staff room is frequently "blue" with smoke. This might be the explanation for the very much higher particulate level, as well as the elevated NO_2 level. The indoor locations in schools were, except for this example, always chosen to be in a classroom, for obvious reasons.

Results.

Although the study is not yet complete, some preliminary results are already available. It is clear that significant gradients in air quality exist across the city of Hamilton. If outdoor air quality were the only variable in the breathing environment of the children, its interrelationship with health effects would be relatively easy to define. However there are several "confounding variables" which we already know have some impact on respiratory health, such as the use of gas for domestic cooking, smoking in the home, number of children in the same room, and family income. In all cases, the distribution of these confounding variables is such as to produce potential adverse health effects in the same direction as that of increasing pollution levels. Thus in the final analysis of this study we must take great care in allowing for the effects of these confounding variables, in order not to inappropriately attribute a burden of negative health effect to air pollution.

The project is currently nearing the end of its last data-gathering year, and there will be a further six months of data analysis at the end. Our ultimate aim is to produce a list of a dozen or so factors in the breathing environment that can be shown to have a negative health effect, and a percentage of the burden attributable to each factor.

Funding.

This project is being supported by: Canada, Health and Welfare; Ontario Ministry of the Environment, and Ministry of Health.

Table I Twenty-four hour sample - Highview School

Day - June 24, 1981

Location	SO ₂ (ppb)	NO ₂ (ppb)	Particulate µg/m ³
Classroom	2.0	22	165
Staff room	1.0	35	2659
Outside	3.0	22	163
HI-VOL TSP	-	-	127
PSD total load	-	-	158

Figure I

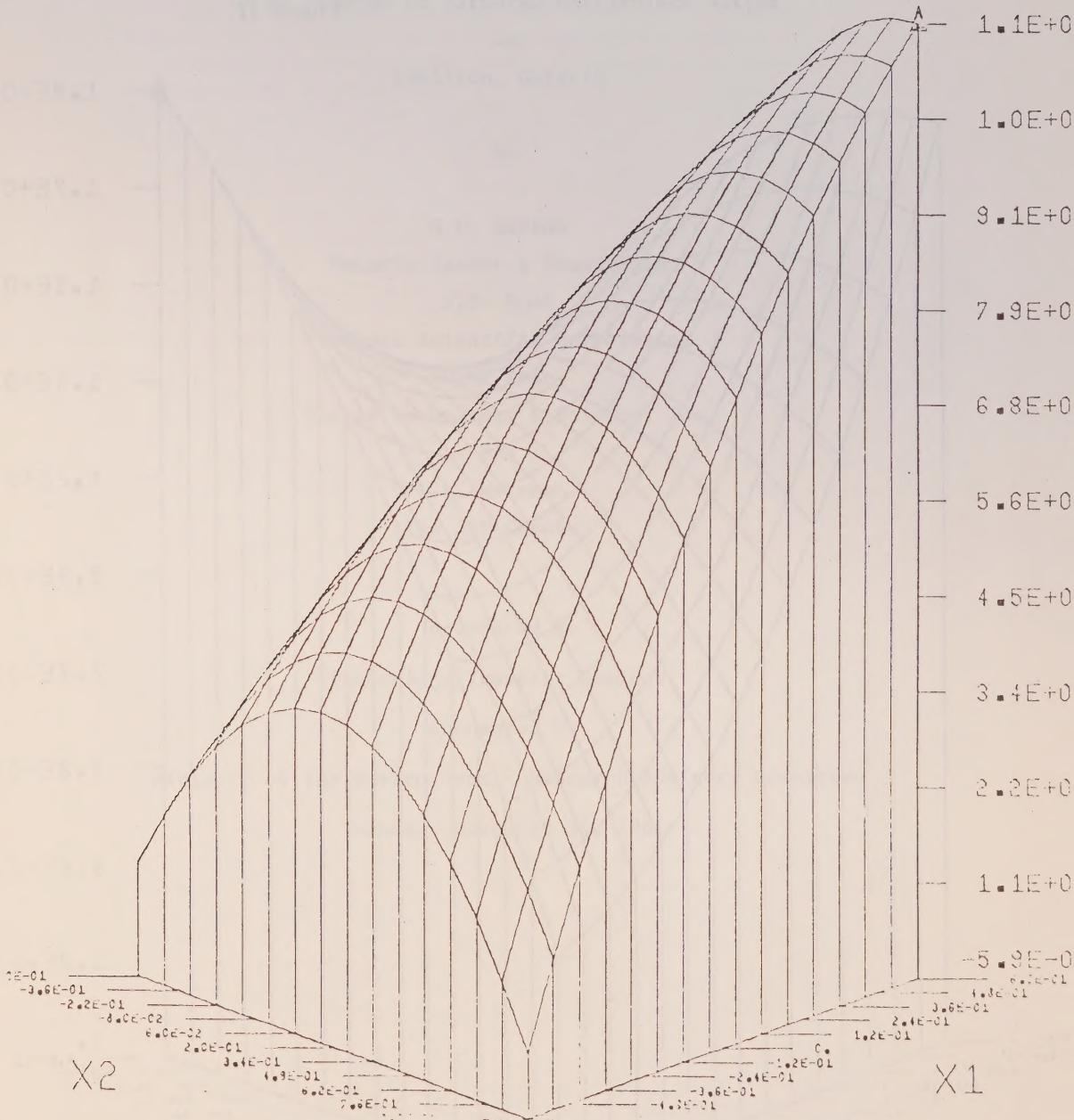
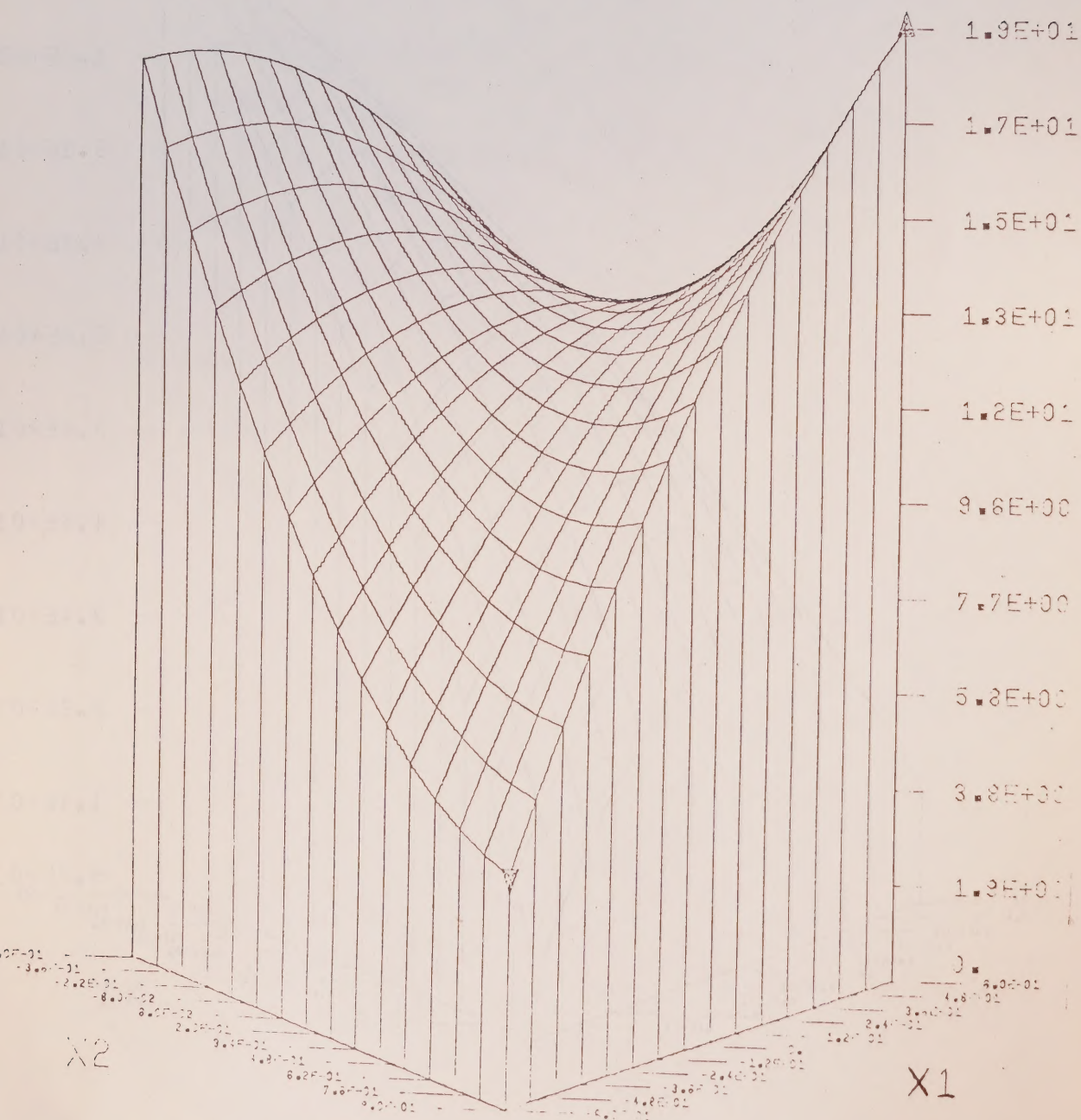


Figure II



An Assessment of Street Dust
and
Other Sources of Airborne Particulate Matter
in
Hamilton, Ontario

by

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Ontario Research Foundation
J.E. Hunt
Concord Scientific Corporation
D.M. Kane
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presented at

Technology Transfer Seminar

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ABSTRACT

Traditional industrial sources of particulate matter have been subjected to increasingly stringent regulations during recent years and significant reductions in total suspended particulate matter (TSP) concentrations have been achieved in most industrialized cities. However, trends in ambient TSP levels indicate that, despite continuing abatement efforts by industry, TSP air quality objectives may not be realized through control of only traditional industrial sources. Hence there is a need to assess the relative impact of other sources, such as particle re-entrainment caused by wind and traffic, on the observed TSP loadings in urban areas. A comprehensive study designed to characterize atmospheric particulate matter, define the importance of various source types, and evaluate street cleaning methods was initiated in 1979 in Hamilton, Ontario, a city of 500,000 in population which contains the largest steel complex in Canada.

Detailed studies of TSP loadings at several sites in Hamilton were conducted over a 3-month period. In addition to assessing the general features of the data, the collected samples were analyzed for a broad range of chemical constituents. These results, as well as dispersion and receptor models, have been used to characterize particulate matter and to assess in detail the relative contribution of various source types to TSP loadings in the Hamilton area.

Road dust and other traffic related sources were the largest contributor ($\sim 40\%$) to TSP levels during the study period followed by background transport of particles into the area ($\sim 35\%$), and general area sources ($\sim 18\%$). Point sources were found to contribute only $\sim 7\%$ despite their obvious presence and significant impact under certain meteorological conditions. The evaluation of street cleaning methods showed that more frequent mechanical sweeping had no measurable effect on TSP levels. A small decrease appears to have occurred as a result of more frequent vacuum sweeping, but statistical tests suggest that the observed change is only of marginal significance. Thus, under most circumstances, more frequent sweeping of roads and streets is unlikely to be a cost-effective approach to achieving significant reductions in urban TSP levels. The results of the Hamilton study have been used to define those experimental approaches suitable for use in future assessments of urban particulate matter.

1. INTRODUCTION

During the past 20 to 30 years, measured ambient suspended particulate matter levels have declined significantly in North America (1-6). This has been achieved largely as a result of increasingly improved controls on particle emissions from industrial point sources. However, analysis of trends in TSP levels indicates that in many urban areas TSP air quality objectives may not be realized through control of these traditional sources alone. Although these observed trends in TSP levels are strongly influenced by local meteorological conditions it seems probable that other sources of particulate matter can make a significant contribution to urban TSP levels. These may prevent the attainment of TSP air quality objectives.

The City of Hamilton, Ontario, was selected as a good urban site in which to carry out a study of urban particulate matter. The city has a population of about 500,000, is located on the south-west shore of Lake Ontario and has the largest steel complex in Canada. Air quality data from the Ontario Ministry of the Environment (MOE) indicate that TSP levels decreased from an airshed average annual geometric mean of $131 \mu\text{g}/\text{m}^3$ in 1970 to an average of $79 \mu\text{g}/\text{m}^3$ over the period 1976-1979 (a 40% reduction); whereas measured and estimated point source emissions in the Hamilton airshed dropped from 2.5×10^7 kg/year in 1970 to 7.3×10^6 kg/year in 1979 (a 71% reduction) (7-9).

A study was undertaken to develop a better understanding of the predominant factors determining particulate matter concentrations in Hamilton and to evaluate the impact of street sweeping methodologies. A general outline of the experimental program, results, and conclusions are presented here. Further details are available in the full report submitted to the sponsoring government agencies and industries (10).

2. EXPERIMENTAL PROGRAM

An intensive program of air quality monitoring was carried out at seven locations (four urban, and three rural). TSP levels were monitored over 6-hour periods at most sites on a 24 hour per day basis for three months. The location of sampling sites is shown on a map of Hamilton in Figure 1. Vertical and horizontal profiles were obtained by locating samples at 3 distances from the roadway and at 3 heights on 15 m towers (Figure 2). At the two major sites (the experimental site, and the control site) other air quality parameters measured included carbon monoxide, coefficient of haze, particle sizing using dichotomous samplers, dust fall, traffic counts, and wind velocity. The general features of the experimental site are shown in Figure 3. Samples of road dust were obtained at a number of the monitoring locations to characterize this potential source of airborne particles.

At the experimental site the study was subdivided into three periods. A baseline period was used to establish statistical equivalence between the experimental and control sites, a mechanical sweeping period was used to assess the effect of daily mechanical road sweeping and a final vacuum sweeping period was used to assess the effect of daily

vacuum road cleaning. During the latter two periods the control site data were used as statistical references.

Filter samples were analyzed for mass loading to obtain TSP and particle size data. Also a wide range of elements were measured using such methods as X-ray fluorescence spectroscopy, ion chromatography, atomic absorption spectroscopy, neutron activation analysis and optical microscopy.

3. DATA ANALYSIS

The data were analyzed for general features such as temporal and spatial patterns, wind and concentration roses, dosage roses etc. In addition, three source apportionment methods were applied to attempt a quantitative assignment of observed TSP levels to contributing source categories.

Microinventory

A microinventory is a detailed compilation of local particle emission sources over an area sufficiently large to include all sources having significant effects on TSP at the receptor site of interest. This inventory includes point and areas sources and requires a comprehensive area inspection to document land use patterns and activity levels which are used to derive fugitive emissions. The result is a compilation of emissions sorted by category and spatial patterns with respect to the receptor of concern. These data are then weighted by category using empirical formulations to take into account directions and distances of sources from the receptor and prevailing meteorological statistics. Finally, the weighted emissions for each category are applied to an empirical equation which relates the expected annual geometric average TSP at the receptor site to the emission data. This procedure was developed by Pace (11) and the empirical equations were calibrated and validated for several U.S. urban areas. The method, although largely empirical, has been shown to be very useful and accurate in predicting annual geometric average TSP levels, although the apportionment of TSP to source category is somewhat less certain. A microinventory was prepared for each monitored location during the study.

Dispersion Modelling

The modelling of transport and diffusion of pollutants emitted into the atmosphere is a frequently used procedure to assess the impact of a source on a given receptor. Required data include a source inventory, meteorological data, source-receptor spatial relationships and local topographic features. An urban model developed by the U.S.-E.P.A. was selected for use in this study (12). This gaussian-plume algorithm uses emission data grouped by point, area, and line sources. Modifications to the line source component along the lines suggested by Rao and Keenan (13) were used.

Chemical Mass Balance (CMB)

This technique is a form of receptor model in which the relative elemental concentrations in emissions from each contributing source (the source elemental matrices) are combined in a linear combination to produce a best fit to the observed relative elemental concentrations at the receptor (receptor elemental matrix). The basic principles of the CMB method were first presented by Friedlander (14, 15). Further developments of this and other receptor models have been recently discussed by Cooper and Watson (16).

Basically, the CMB method is the only receptor model that makes direct use of detailed chemical composition information in connecting specific sources or types of sources with ambient particle loadings. By itself the method is not capable of distinguishing sources having similar elemental emission patterns. Such sources are grouped into single source types.

The most significant limitation to source resolution with the CMB method is the uncertainty in the source elemental matrices. A total of fourteen source fingerprints were selected for possible fitting to the receptor data. The source elemental matrices were taken largely from published data and source characterization studies carried out elsewhere, because of the general lack of quantitative elemental analyses of point source emissions in the Hamilton area. This aspect of the study is currently being studied in further detail before submission of the final report. The study was enhanced by the collection and analysis of road dust samples in the Hamilton study area in order to provide a good elemental matrix for this particular source.

4. RESULTS AND DISCUSSION

A large data base of meteorological measurements, air quality conditions and about 5,000 filter samples were analyzed.

The general characteristics of the data were consistent with previous studies and area air quality data reported by MOE from on-going monitoring programs. Diurnal variations, the dependence of TSP on various meteorological parameters, wind and pollution roses, and dosage roses were all consistent from site to site. TSP data were log-normally distributed confirming that none of the sites were predominately influenced by a specific local source of particles. The influence of emissions from the heavily industrialized area of Hamilton were apparent under appropriate meteorological conditions. The experimental and control sites were found to be similar in a statistical sense.

Source apportionment data were derived from the microinventory, CMB and dispersion modelling methods. In order to provide a useful compilation for comparison, the sources were grouped into four categories; area, point, traffic-related and background. For the purpose of this summary, traffic related emissions are expressed separately from area sources. This traffic-related source also includes road dust which may be re-entrained as a result of general wind action on roads, parking lots or laneways etc. Point sources are predominately steel

manufacturing related. The background source represents particulate matter transported into the Hamilton urban area from outside the city.

The source apportionment data as determined by the three methods agreed remarkably well. The results for the experimental site are summarized below.

<u>Source</u>	<u>Percent Contribution</u>		
	<u>Microinventory</u>	<u>CMB</u>	<u>Dispersion Model</u>
Area	18	16	19
Point	2	8	6
Traffic-Related	46	38	40
Background	34	20	35

Traffic-related sources are the largest contributing category at an average of 40%. This is made up of about 25% from road dust and 15% from vehicular exhaust emissions.

The second largest category is the background source. For the microinventory and the dispersion model this was determined primarily as a result of data obtained from background TSP monitoring sites. The figure of 35% is consistent with other studies concerned with the background TSP levels in Hamilton and elsewhere. The CMB method as used here does not provide an estimate of the background contribution to TSP. The figure of 20% represents the "excess" sulphate expressed as ammonium sulphate which is expected to originate primarily from long range transport into the area. Other anticipated background components include nitrates and organic material. These were not determined in the chemical analysis applied to the CMB but could reasonably be expected to account for most of the remaining 15% in the CMB background source contribution.

Area sources contributed an average of about 18% to the TSP. This significant amount is substantially larger than the point source contribution which was the smallest of the categories at an average of about 7%.

It should be kept in mind that these data represent average contributions taken over the study period. Source apportionment figures for specific events vary considerably and where averages over different time periods are required these data may not be appropriate. This type of extrapolation can be carried out using an approach along the lines of the Portland Aerosol Characterization Study (17). In this study source apportionment data were accumulated for a variety of meteorological conditions. Based on these data and the frequency of occurrence of the classes of meteorological conditions over the time span of interest, a period average source apportionment can be calculated.

The street sweeping experiments allowed an evaluation of the effectiveness of increased frequency of mechanical and vacuum cleaning. During the baseline period no special additional cleaning procedures

were carried out and a statistical analysis showed that the experimental and control sites were not significantly different from each other with respect to TSP values and other parameters observed. During the mechanical sweeping period the experimental site area was cleaned daily with a mechanical street sweeper. Although TSP levels were found to be higher at the experimental site during this period the same was observed at the control site and it is concluded that there was no statistically significant effect on observed TSP values at the experimental site attributable to an increased frequency of mechanical sweeping. During the vacuum sweeping period (daily frequency) the TSP values were found to be somewhat lower at the experimental site than the control site. This difference was, however, found to be only of marginal statistical significance. A statistical evaluation of the data for a specific set of conditions which can be expected to provide a more sensitive test of the impact of re-entrained road dust on TSP levels showed no significant difference between the experimental and control sites. This was confirmed by the CMB results for the period. However, it should be noted that, due to variability in the data, a 30 - 40% reduction in the road dust contribution to the observed TSP values would be required in order to produce a statistically significant reduction in TSP. This corresponds to a TSP change of from 5 to 10 $\mu\text{g}/\text{m}^3$.

Thus, although there are valid reasons for urban street cleaning (e.g. aesthetic effects), more frequent sweeping of roads and streets is unlikely to be a cost-effective approach in the control of airborne particulate matter in most urban areas unless undertaken as part of a comprehensive program which addresses all significant source categories.

5. ACKNOWLEDGEMENTS

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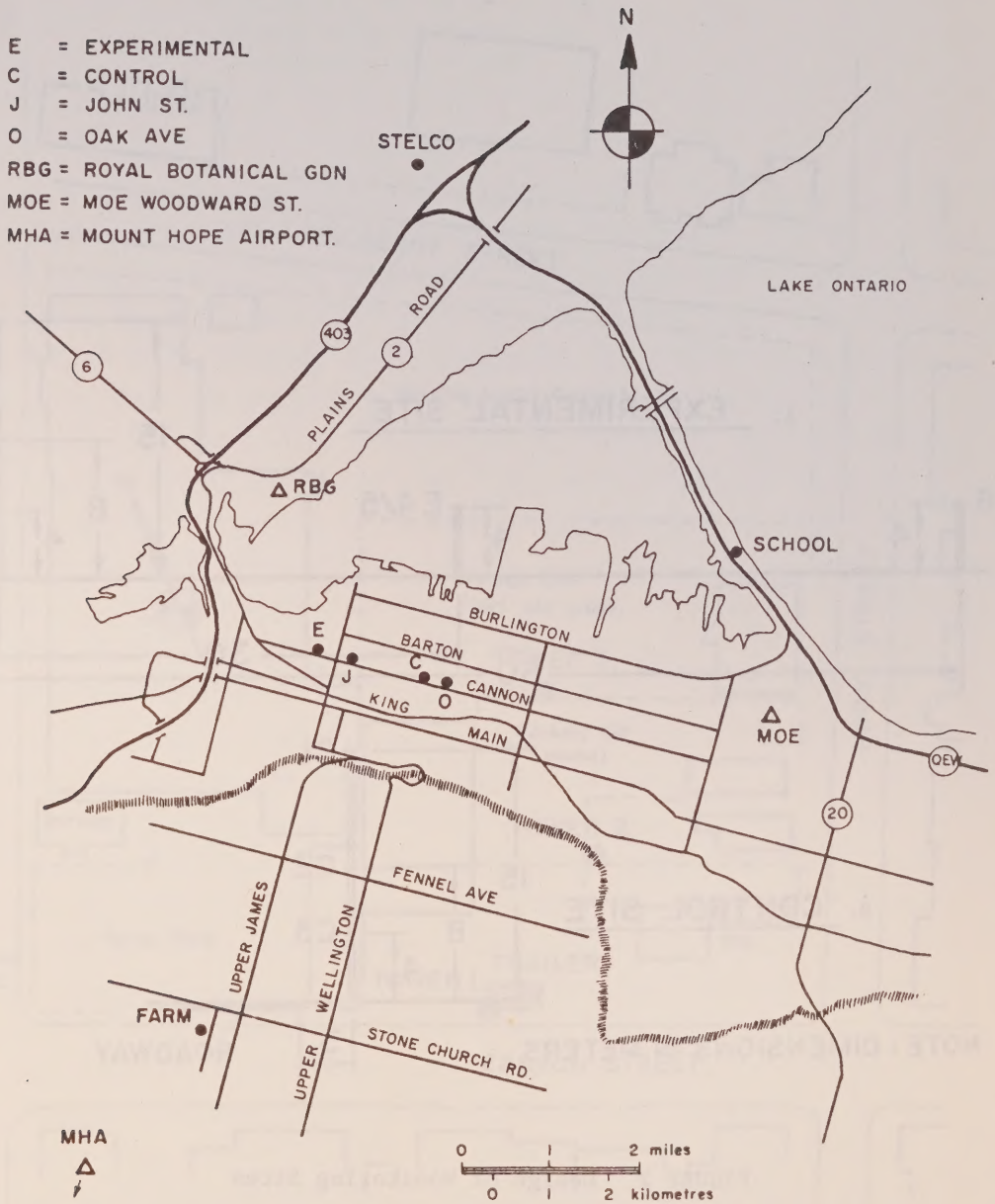


FIGURE 1 MAP OF HAMILTON AREA

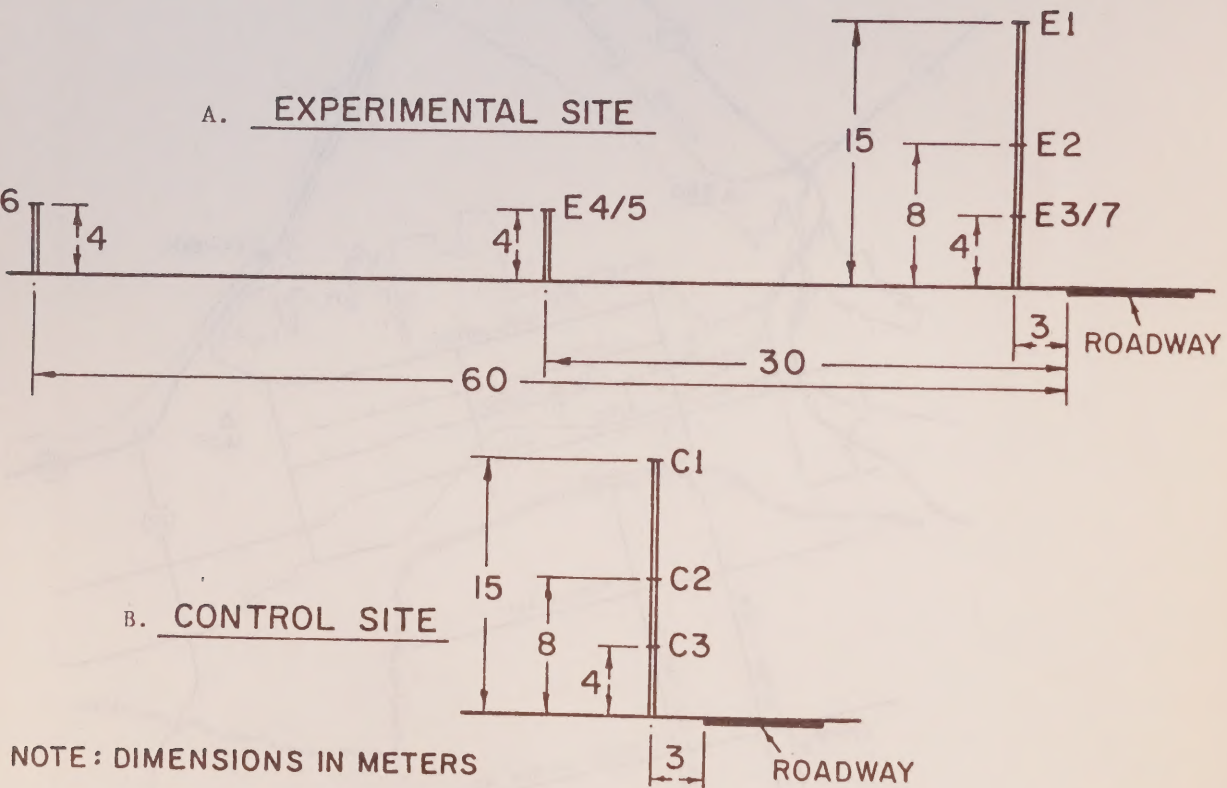


FIGURE 2 Design of Monitoring Sites

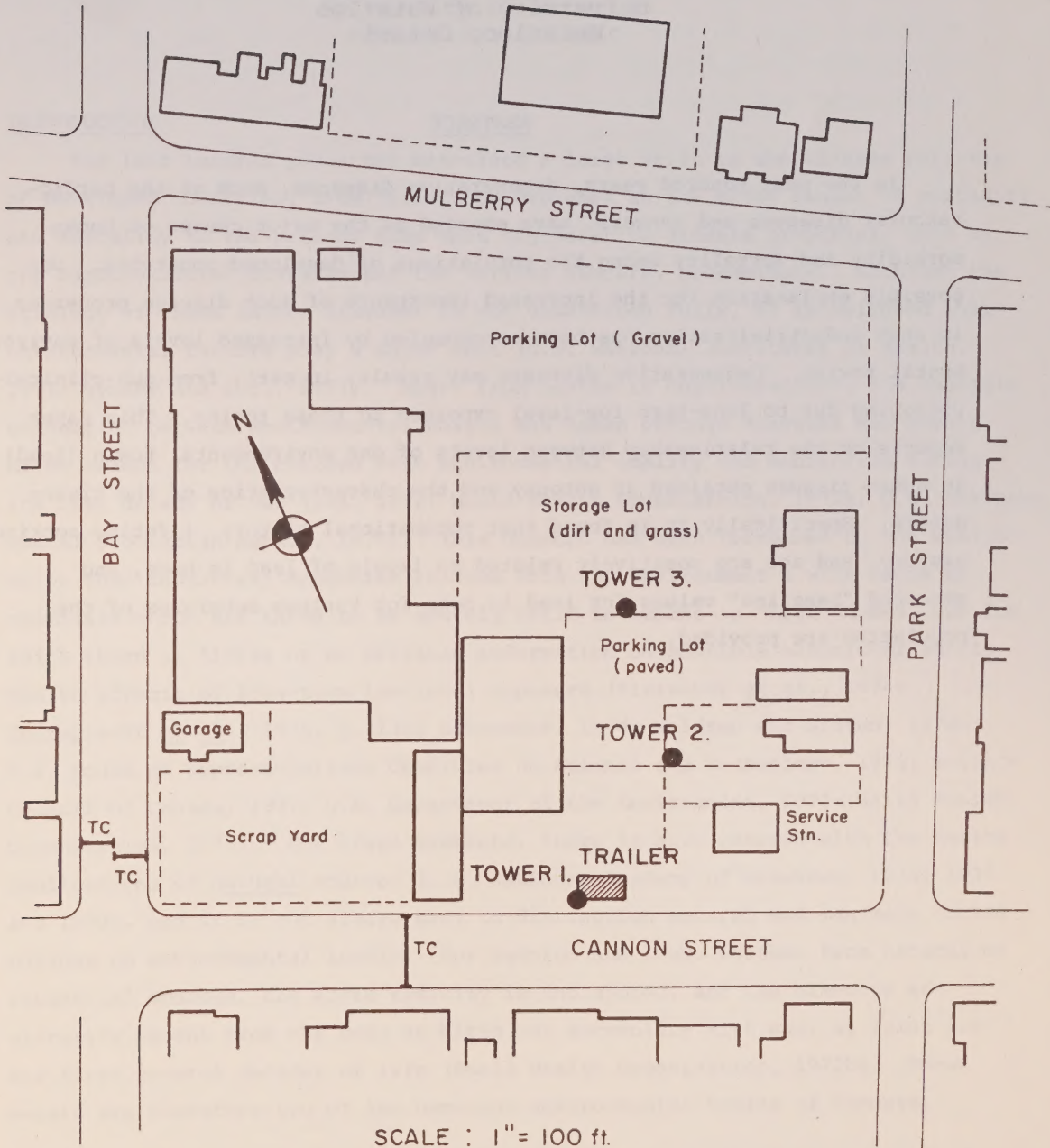


FIGURE 3 EXPERIMENTAL SITE

LEAD AND CADMIUM VALUES IN AUTOPSY MATERIAL

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ABSTRACT

In the past hundred years, degenerative diseases, such as the cardiovascular diseases and cancers, have emerged as the major causes of human morbidity and mortality among the populations of developed countries. One possible explanation for the increased importance of such disease processes is that industrialization has been accompanied by increased levels of environmental toxins. Degenerative diseases may result, in part, from sub-clinical poisoning due to long-term low-level exposure to these toxins. This paper reports on the relationship between levels of one environmental toxin (lead) in human tissues obtained at autopsy and the characteristics of the tissue donors. Specifically it is found that occupational history, lifetime smoking history, and age are positively related to levels of lead in bone, and smoothed "baseline" values for lead in bone for various subgroups of the population are provided.

LEAD AND CADMIUM VALUES IN AUTOPSY MATERIAL

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INTRODUCTION

The last hundred years has witnessed a large shift in the disease patterns of developed countries, from infectious diseases as the major causes of morbidity and mortality to the present time when degenerative disease processes, such as the cardiovascular diseases and the various cancers, predominate. Although the etiology of these latter diseases is not understood fully, it is believed that environmental factors play a major role (U.S. National Institutes of Health, 1971; Wynder and Gori, 1977). Apart from aesthetic considerations, the possible connection between environmental toxins and human chronic diseases has been a major reason for the concern with environmental quality and monitoring during the last decade or two (Lee, 1972; World Health Organization, 1972a; U.S. Environmental Protection Agency, 1976). This concern has been increased by the realization that industrial economies release into the environment a wide range of chemicals which are known to be acutely toxic to humans in "high" doses, but for which there is little or no reliable information on possible chronic or subtle health effects of long-term low-level exposure (Fleischer et al., 1974; Indraprasit et al., 1974, p. 135; Schroeder, 1974; Waldron and Stöfen, 1974; U.S. House of Representatives Committee on Science and Technology, 1976; Science Council of Canada, 1977; U.K. Department of the Environment, 1977; World Health Organization, 1977). For trace elements, there is also concern with the health implications of natural sources (U.S. National Academy of Sciences, 1974, 1977 and 1978), and it is not always easy to distinguish natural and man-made contributions to environmental levels. For cadmium and lead, whether from natural or industrial sources, the acute toxicity is undisputed, and the elements are virtually absent from the body at birth but accumulate with age, at least for the first several decades of life (World Health Organization, 1972b). These metals are therefore two of the numerous environmental toxins of concern.

In assessing the human health implications of environmental cadmium and lead, the measurement of levels in human tissues is relevant for a number of reasons. First, the determination of levels, in appropriate tissue(s), is

necessary to quantify cadmium and lead absorption from the general environment. These data can also be used to estimate "normal" levels in human tissues and to provide baselines for future biological monitoring; in addition, they can allow estimates to be made of the biological half-life of cadmium and lead in different organs (e.g., Elinder et al., 1976). Secondly, measurement of cadmium and lead levels in occupationally exposed individuals is an important component of a program of industrial hygiene. Such data may also indicate differences in response of the human organism to higher, rather than lower, environmental levels, and may suggest the safety margin between current general environmental levels and concentrations at which clinical symptoms of poisoning begin to appear, particularly in more susceptible or high-risk individuals. Thirdly, if tissue cadmium and lead levels are measured in individuals for whom appropriate medical and personal histories are available, it is usually possible to identify at least some of the factors (e.g., age, cigarette smoking) which are associated with increased levels in the general population. A knowledge of these factors may then suggest ways of reducing exposure. More generally, it may be possible to use such data in epidemiological studies to search for relatively subtle changes in patterns of morbidity or mortality, and hence to estimate threshold levels of cadmium and lead in a particular tissue for the appearance of significant deleterious human health effects (cf. Fleischer et al., 1974, pp. 297-301). For cadmium, a tentative threshold level in human renal cortex has been suggested as 200 $\mu\text{g/g}$ wet weight by Friberg et al. (1974, p. 114) and by a WHO Task Group (1977), but has been criticized by Nomiyama (1977) and by Brown et al. (1978). In addition, Piscator (1973) has indicated some of the uncertainties involved in setting this figure and has emphasized the limited safety margin between it and the cadmium levels observed in certain studies, particularly if environmental pollution by cadmium has continued at the level then prevalent or has increased. For lead, the threshold refers to blood, and a level of 0.4 $\mu\text{g/g}$ (i.e., 40 $\mu\text{g}/100\text{ ml}$) is often stated (e.g., U.S. National Academy of Sciences, 1974, p. 55); however, for sensitive population subgroups such as children, a lower threshold (e.g., 0.2 $\mu\text{g/g}$) may be desirable.

It is generally not practicable to estimate directly an individual's exposure to the trace element(s) of interest from sources such as food and beverages, tobacco smoke and air. An alternative is to determine elemental levels in samples of one or more tissues from appropriate donors, and to assume that these levels provide an estimate of exposure; however, metabolic differ-

ences among donors and the chemical (and physical) form(s) of the element(s) to which they are exposed may also be reflected by tissue levels. The next step is to search for differences in elemental levels¹ (or burdens¹) between

¹(Cadmium or lead) "levels" or "concentrations" (usually in units of µg/g) are to be distinguished from the burdens (i.e., the amounts, usually in µg or mg) of these metals in one or more organs or tissues

between the "experimental" and "control" groups of donors; this is often hindered by the presence of other factors which may influence the magnitude and the variability of these levels and which may also, in some instances, affect the donor "response". For example, sex, age and cigarette smoking are (causally?) related to elevated cadmium levels in several soft tissues (e.g., Lewis et al., 1972; LeBaron et al., 1977) and to an increased incidence of cardiovascular disease (e.g., U.S. National Institutes of Health, 1971; U.S. Surgeon General, 1979).

The detection of relevant differences among donors in the presence of "noise" in trace-element data can be facilitated in two ways. First, sources of variability in the elemental data generated in the analytical laboratory should be controlled as far as possible; this includes the use of: proper anatomical sampling schemes(s) for the tissue(s) under investigation, standard samples, independent replicate analyses, standardized conditions for the weight bases on which the elemental levels are expressed, etc. Secondly, it is important to identify donor characteristics (such as sex, age, smoking habits, occupation, place of residence and perhaps medication) which are associated with trace-element levels. It is then usually necessary in the data analysis to adjust or allow for the effects of these characteristics when seeking relationships among the variables of primary interest; suitable data analytic techniques include regression and donor matching. The two sources of variability are also relevant to considerations of the extent to which data derived from "samples" are representative of the corresponding "population"; in the present context, this applies at three levels--samples within the tissue or organ, tissue or organ within the donor and donor within the population.

More details about the above and related matters for cadmium are given in a comprehensive critical review of the human cadmium literature recently published by one of the authors (Cherry, 1981).

THE PRESENT STUDY

The present work is part of an ongoing study (Esterby, 1976; LeBaron, 1977; Brown et al., 1979a; Cherry, 1980; Brown et al., 1979b; Brown et al., 1978; Cherry et al., 1978) into the health effects of long-term exposure to low levels of lead and cadmium. The present publication is mainly concerned with lead. Ideally, to evaluate the long-term health implications of exposure to lead, a group of individuals should be followed until death; indices of trace-metal exposure should be tabulated for each study subject and mortality patterns of these individuals studied to determine health effects of substances under study. Also, samples should be taken at autopsy to determine the distribution of lead in the body and the donor characteristics which are associated with this accumulation. A study of this kind is prohibitive with respect to cost and time required for completion. Hence, in the present study, tissues thought to contain levels of lead which reflect long-term exposure were taken at autopsy from donors and were analyzed to estimate the concentration of lead. The data were obtained from autopsy samples from 368 donors from Ontario and Quebec. For each individual, a subset of the donor information:

- | | |
|--|---------------------|
| (1) Sex | (2) Age at death |
| (3) Height and Weight at Death | (4) Smoking History |
| (5) Primary and Secondary Cause of Death | (6) Occupation |
| (7) Place of Residence | (8) Nationality |
| (9) Clinical Resume and Autopsy Report | |

was available; for details, see Esterby, 1976; LeBaron, 1977; Krailo, 1981.

RESULTS

The purpose of this section is to assess which donor characteristics are related to lead levels in bone. Regression techniques aid in assessing the joint relationship between several concomitant variables and a response variable. In the present situation, the response variable is the lead concentration in section B rib² for the tissue donor and the concomitant variables are donor

²The rib samples were 3 cm sections of rib shaft, taken immediately adjacent to the costal cartilage.

characteristics such as age at death, sex, smoking habit and occupational history.

A summary of the lead concentrations in rib subdivided by sex, smoking history and age is shown in Table 1.

Preliminary analysis of the present data set indicated that the following variables should be taken into consideration when formulating possible regression models:

- (1) sex of donor,
- (2) smoking history of donor,
- (3) age of donor,
- (4) occupational history of donor,
- (5) cause of death of donor.

As noted from the examination of trends in the means and medians from a previous analysis on a subset of the present data set (Krailo et al., 1976), age² and pack-years smoked are variables which should also be considered in any regression.

It has been noted previously that lead uptake in young individuals is much greater than that of older individuals (Goyer and Mahaffey, 1972; Alexander et al., 1972) and also that lead may substitute for calcium in osteogenesis (Greengard, 1966). Hence, variables which identify young individuals (e.g., death before 25 years of age) and which may be an index of calcium in bone (e.g., ash as a fraction of wet weight) will also be considered in the formulation of possible regression models.

Models for Lead Accumulation in Bone

In order to formulate regression models for lead concentration in rib, possible theoretical models for lead accumulation in bone should be examined. For the purposes of this discussion, it will be assumed that the ash weight of bone is approximately constant over a large proportion of the age range of the donors (but cf. Cherry et al., 1975). Thus, the lead concentration in rib will roughly approximate the total amount of lead in bone. It may be hypothesized that the total amount of lead in bone is the result of small increments of lead accumulation each day. With this assumption, the lead level in bone may be represented as:

$$L = \sum_j D_j + \sum_j I_j + \sum_j S_j + \sum_j O_j,$$

where:

- (1) D_j is the amount of lead absorbed from dietary sources such as food and water in a given day, with $D_j \sim N(\mu_D, \sigma_D^2)$.
- (2) I_j is the amount of lead absorbed from inhalation during any given day, with $I_j \sim N(\mu_I, \sigma_I^2)$.
- (3) S_j is the amount of lead absorbed from smoking a cigarette, with $S_j \sim N(\mu_S, \sigma_S^2)$.
- (4) O_j is the amount of lead absorbed via occupational exposure on any given day, with $O_j \sim N(\mu_O, \sigma_O^2)$.

This model implies that the variance of lead concentration should increase with age and that the lead levels of smokers should vary more than those of non-smokers. This pattern is noted in the summary statistics for the various age and smoking subgroups, with the exception of the oldest age group (see Table 1). It would appear that a measure of total smoking exposure (such as pack-years smoked) is useful in explaining the variation in lead levels in rib. Also, age and occupational history should be included in any model for lead levels in rib.

Data Analysis

A list of the concomitant variables (and their identifying numbers) considered in the subsequent analyses is given in Table 2. A Box-Cox analysis of transformations of the response variable (Box and Cox, 1964), lead concentration in section B rib, was undertaken to determine the "best" scale on which to express the data. For the purposes of this analysis, it is assumed that for $y^{(\lambda)}$, some unknown transformation of the original observations, the following model holds:

$$y_i^{(\lambda)} = \beta_0 + \sum_{j=1}^p \beta_j x_{ij} + e_i \quad \text{---- (1)}$$

where

- (1) $y_i^{(\lambda)}$ is the transformed lead concentration (in $\mu\text{g/g}$ ash) in section B rib for the i^{th} individual;
- (2) x_{ij} is the value of the j^{th} donor characteristic for the i^{th} individual, $j = 1, 2, \dots, p$;

- (3) p is the number of donor characteristics examined;
- (4) e_i is a normally distributed random error term with mean 0 and unknown variance σ^2 with e_i and e_j independent for $i \neq j$; and
- (5) β_j is the regression coefficient associated with j^{th} donor characteristic, $j = 1, 2, \dots, p$.

β_j can be regarded as the increase in the expected value of $y_i^{(\lambda)}$ brought about by a 1 unit change in x_{ij} , when all other variables in the model are held constant.

The family of transformations examined for the present analysis is:

$$y^{(\lambda)} = \begin{cases} y^\lambda & \text{for } \lambda \neq 0 \\ \ln(y) & \text{for } \lambda = 0. \end{cases}$$

Because the model for lead accumulation proposed above implies that smokers and non-smokers have generally different variances of lead levels in bone, Box-Cox analyses were carried out on the data subdivided by sex and smoking habit as well as on the entire data set.

Before this procedure was employed, various values of λ were selected. Multiple linear regression was performed using the transformed observations and all relevant independent variables, so that outliers could be detected.

Using a Q-Q plot, the residuals $\hat{e}_i = y_i^{(\lambda)} - (\hat{\beta}_0 + \sum_{j=1}^p \hat{\beta}_j x_{ij})$ were

examined to identify individuals with "unusual" exposures to lead. If equation 1 is true for all individuals in the sub-group, this plot should be approximately a straight line with slope σ and intercept 0. Residuals which deviate appreciably from this line indicate donors that may have had exposure to lead not accounted for by the variables included in the regression model. The clinical resumé of each of these individuals was therefore examined for indications of unusual lead exposure. If such evidence was found, or if there was doubt as to the validity of the values of the associated variables, the individual was excluded from further analysis. If no evidence could be found to indicate that the donor had unusual lead exposure, but the inclusion of this donor changed significantly the fitted regression model (for example, by

changing the sign and significance of some of the coefficients), this individual was also removed. However, an effort was made to obtain additional donor information on these individuals to find possible reasons for the large residual not accounted for by the donor information presently available. If inclusion of the "outlier" did not substantially affect the regression model, the individual was retained in the analysis.

After the "best" scale for expression of the response variable was determined, a "best subsets" analysis, using the C_p statistic as selection criterion, was employed (e.g., Daniel and Wood, 1971). This procedure led to the selection of a few models which adequately described the data. Terms which appeared in all competing models were considered important in predicting lead concentration in rib. From among these models, a "final" model was chosen by examining significance levels, the R^2 statistic and residual plots.

The results obtained using the transformation indicated by the Box-Cox analysis were also compared with the results of a C_p analysis of regressions performed on the untransformed data.

The numbers of donors available for regression analysis in each subgroup are given in Table 1. It may be noted that, whereas all non-smokers are available for regression, only a proportion of the smokers and ex-smokers are available for regression. It is also interesting to note that the proportion of smokers and ex-smokers with complete donor documentation decreases with increasing age.

Q-Q plots of the residuals from the regressions using various λ revealed 7 possible outliers on all scales. The observed values of lead concentration in rib for 5 of these individuals were much greater than the predicted values and the remaining two individuals had observed values substantially lower than the predicted values. One of the individuals with unusually large observed values displayed some symptoms of clinical lead poisoning, (i.e., hypocoagulability), but did not have lead poisoning entered on his clinical resumé. For the remaining six donors with anomolous lead values, no explanation could be found from their histories. All the outliers were eliminated from further analysis, because the significance level and/or the sign of some of the coefficients was affected by their inclusion.

A Box-Cox analysis of transformations of lead concentration in rib was performed as described above. When performing this analysis on the data subdivided by sex and smoking habit, some variables could not be examined in certain subgroups (see Table 3). The log-likelihoods for the full data set and the data set segregated by sex and smoking habit have maximums close to $\lambda = 0$, (i.e., the logarithmic transformation). In both instances, an approximate 95 per cent confidence interval for λ does not contain $\lambda = 1$ (untransformed data). The likelihoods for the individual subgroups yielded similar results, with the likelihoods for the female smokers and male ex-smokers (the two subgroups with the smallest number of observations) having wider confidence intervals than those associated with the other subgroups. This is consistent with the logarithmic transformation being the "best" transformation of the data. The log-normal model has been used by other investigators to describe trace-element concentrations in various human tissues (Gross et al., 1975; LeBaron, 1977; Billick et al., 1979). However, with the exception of LeBaron (1977), the data was not adjusted for concomitant variables.

Since the model given above indicates that there may be heteroscedasticity between smoking and non-smoking subgroups of the population, Bartlett's test for equality of intersubgroup variances was performed on the regressions using the transformed data. The resultant test statistic, which is asymptotically distributed as a $\chi^2_{(4)}$ random variable, had an observed value of 7.51 (associated significance level = 0.11). Thus, there is no strong evidence of intersubgroup heteroscedasticity and hence the analysis was performed on the full data set. It is interesting to note that, when the data are expressed on the natural scale, the test statistic for equality of intersubgroup variance had an observed value of 31.12, with corresponding significance level less than 0.001. This indicates that, on this scale, there are differences in the intersubgroup variance, as predicted by the model proposed above.

A best subsets analysis of the full data set (expressed on the logarithmic scale) was done to determine the variables significantly related to the response variable (see Tables 4 and 5). The results indicate that, after adjusting for other variables, log lead concentration in rib is positively associated with pack-years smoked, age, ash weight of section B rib, and the indicator variables "donor is male" and "donor was employed in an occupation classified as exposed";

the response variable is negatively associated with years smoked, age², ash as a fraction of wet weight of section B rib and the indicator variables "donor was an ex-smoker" and "donor was a non-smoker".

The results obtained from the untransformed data are similar. From this analysis, it may be noted that lead levels in rib are positively related to pack-years smoked, age^{1/2}, ash weight of section B rib and the indicator variables "donor was employed in an occupation classified as exposed" and "donor died of cancer"; lead levels in rib are negatively related to ash as a fraction of wet weight of section B rib and the indicator variables "donor was an ex-smoker" and "birth year of donor was after 1920". Since Bartlett's test for the equality of subgroup variances demonstrated that the subgroup variances for the regressions based on the natural scale were significantly different, an analysis of the data segregated by sex and smoking status was also carried out. The results are summarized in Table 6.

The residual plots (Q-Q plots and scatter plots of the residuals, standardized by their approximate standard deviations, graphed against predicted values and age) demonstrated that the transformed data appear to satisfy the assumption of normality and homoscedasticity of the errors. This is not the case for the untransformed data. Scatter plots of the residuals graphed against age and predicted values indicate an increase in variance with both age and predicted value. A Q-Q plot of the residuals indicates significant deviations from a straight line.

The final model (transformed data) was used to determine "smoothed" baselines, i.e., predicted average lead levels in rib for various subgroups of the population (see Table 7). To construct this table, the following assumptions were made:

- (1) ash weight was assumed to be the study population average (0.61822 g);
- (2) ash as a fraction of wet weight was assumed to be the study population average (0.23561);
- (3) smokers were assumed to have started smoking at 15 years of age.

The table was constructed using the midpoint of each age group and an appropriate smoking classification. 95 per cent confidence intervals for a single future observation for an individual in a given subgroup are also displayed in Table 7. As there were no occupationally exposed females in the study popula-

tion, smoothed baselines were not calculated for this subgroup.

DISCUSSION

The Box-Cox analysis indicates that log concentration is the "best" response variable to use for regression analysis. As the logarithm is a monotone increasing function, the regression analysis of the transformed data may be interpreted as follows:

- (1) A history of occupational exposure to lead is associated with elevated levels of lead in bone, when all other variables are held constant.
- (2) For smokers and ex-smokers, an increase in the number of pack-years smoked implies an increase in lead levels in rib, when all other variables are held constant.
- (3) Ex-smokers have lower levels of bone lead than comparable smokers, i.e., smokers with values of the other concomitant variables identical to those of the ex-smokers under consideration. Non-smokers have an even lower level of lead than a "comparable" smoker, i.e., a smoker with 0 pack-years smoked.
- (4) There is a non-linear positive association between lead levels in rib and age. This nonlinear association may arise because of:
 - (i) a cohort effect -- older individuals in the study may have been exposed to less lead early in their lives than the younger individuals in the study.
 - (ii) a selection effect -- individuals with higher lead levels tend to die at younger ages.
 - (iii) an artifact of the method of lead accumulation in bone -- lead may accumulate more slowly when there is more lead present in the bone, as in older individuals.
- (5) Ash weight of section B rib and years smoked are positively and negatively related to lead levels in rib, respectively. These terms may be a reflection of age; e.g., the youngest individuals in the study had lower bone ash weights than the older individuals in the study.
- (6) The model indicates that males have generally higher lead levels than females. This may be a reflection of occupational exposure

not quantified by the 0-1 nature of variable 1, "donor was employed in an occupation exposed to lead".

- (7) Ash as a fraction of wet weight is negatively related to lead levels in rib. This may be because lead can substitute for calcium in osteogenesis (Greengard, 1966), and calcium is the major constituent of bone ash.

The results for the untransformed data are similar to those described above. The variable $\text{age}^{\frac{1}{2}}$ appears instead of the linear and quadratic terms in age. The variable 15 "cancer death" appears to be significantly related to lead levels only in the male smokers, but all individuals dying of cancer in this subgroup died of lung or bronchopharengeal cancer. Thus, the relationship may be because of some facet of smoking behaviour not measured by the variables presently incorporated in the model.

The logarithmic transformation gives a scale on which the data satisfy the assumptions of linearity of response to the independent variables and homoscedasticity and normality of errors. Specifically, this transformation reduces heteroscedasticity with age and between subgroups. Also, the transformation may reduce some skewness in the distribution of the residuals. It may also be noted that there is a greater proportion of the total variation accounted for by the independent variables by regression on the transformed data than by regression on the untransformed data.

It is interesting to note that the theoretical model given above indicates that the variance in lead levels increases with age, smoking consumption and occupational exposure to lead. If the data could be weighted to account for these factors, some of the heteroscedasticity in the untransformed data may be reduced. Also, if such weighting could be found, it might be helpful in the modelling of lead accumulation in rib. Unfortunately, data on dietary habits and details of occupational exposure to lead such as length of employment and information on lead levels at the place of employment is not presently available.

Although the logarithmic transformation implies that the data expressed on an untransformed scale are related multiplicatively to the independent variables, the model should not necessarily be interpreted in that sense. The transformed regression model may be viewed as being descriptive; that is, the

regression analysis identifies the factors which are jointly related to lead levels in rib, and, to some extent, the form of that relationship. The transformation of the data may not be necessary if more information regarding donor characteristics such as diet were available and if a weighting function for the observations could be found. It should be noted that additional information regarding donor characteristics may reduce the importance of the age-related terms in the model.

CONCLUSIONS

The analysis of the joint action of the concomitant variables considered indicates that age, occupational history and lifetime smoking exposure are related positively to lead levels in rib. Also, it appears that the logarithmic transformation of the data is necessary for the data to conform to the assumptions of linearity of expectation in the independent variables and homoscedasticity and normality of the residuals.

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Table 1. Lead Concentration in Rib[†] by Sex, Smoking History, and Age

NON-SMOKERS						SMOKERS						EX-SMOKERS					
AGE GROUP	n*	SAMPLE MEAN	SEM	RANGE	AGE GROUP	n*	SAMPLE MEAN	SEM	RANGE	AGE GROUP	n*	SAMPLE MEAN	SEM	RANGE	AGE GROUP	n*	RANGE
0-34	5(5)	5.35	0.76	2.37- 6.58	0-34	11(8)	19.98	2.50	9.71- 32.61	0-34	3(1)	14.86	2.82	9.42- 18.92	0-34	3(1)	14.86
35-44	2(2)	34.38	4.03	30.34- 38.41	35-44	10(8)	23.44	1.97	15.40- 33.70	35-44	3(3)	22.94	1.91	19.30- 25.75	35-44	3(3)	22.94
45-54	9(9)	21.82	3.06	12.76- 43.36	45-54	43(36)	32.91	2.45	15.05- 88.02	45-54	6(6)	26.05	3.33	16.41- 34.72	45-54	6(6)	26.05
55-64	10(10)	21.46	3.28	10.72- 43.37	55-64	34(20)	36.69	3.65	15.90-104.59	55-64	15(11)	35.28	3.56	17.69- 62.41	55-64	15(11)	35.28
65-74	6(6)	28.43	3.29	18.42- 39.98	65-74	23(11)	29.19	2.59	8.59- 62.00	65-74	10(4)	34.68	7.71	13.77-100.39	65-74	10(4)	34.68
75+	5(5)	35.94	12.66	20.62- 86.39	75+	8(4)	35.90	3.74	26.96- 57.00	75+	5(1)	25.44	5.73	9.87- 42.35	75+	5(1)	25.44
OVERALL	37(37)	23.15	2.46	2.37- 86.39	OVERALL	129(87)	31.59	1.44	8.59-104.59	OVERALL	42(26)	30.31	2.50	9.42-100.39	OVERALL	42(26)	30.31
0-34	2(2)	3.85	3.81	2.62- 5.07	0-34	3(2)	13.92	3.05	9.49- 19.76	0-34	3(2)	13.92	3.05	9.49- 19.76	0-34	3(2)	13.92
35-44	3(3)	12.82	1.95	9.19- 15.87	35-44	10(7)	17.90	2.38	9.75- 33.68	35-44	10(7)	17.90	2.38	9.75- 33.68	35-44	10(7)	17.90
45-54	8(8)	20.29	4.38	8.14- 45.35	45-54	10(8)	23.06	2.76	10.87- 37.60	45-54	10(8)	23.06	2.76	10.87- 37.60	45-54	10(8)	23.06
55-64	19(19)	22.40	1.95	12.84- 46.89	55-64	15(6)	33.10	3.50	15.71- 68.82	55-64	15(6)	33.10	3.50	15.71- 68.82	55-64	15(6)	33.10
65-74	16(16)	21.74	2.24	10.06- 38.08	65-74	10(6)	29.91	4.15	15.00- 63.26	65-74	10(6)	29.91	4.15	15.00- 63.26	65-74	10(6)	29.91
75+	7(7)	26.80	5.56	15.60- 57.42	75+	0(0)	---	---	---	75+	0(0)	---	---	---	75+	0(0)	---
OVERALL	55(55)	21.27	1.42	2.62- 57.42	OVERALL	48(29)	25.98	1.82	9.49- 68.82	OVERALL	48(29)	25.98	1.82	9.49- 68.82	OVERALL	48(29)	25.98

* Numbers in brackets represent the number of donors with complete donor documentation.

† The rib samples were 3 cm sections ("Section B") of rib shaft, taken immediately adjacent to the costal cartilage.

n Number of tissue donors.

SEM Standard error of the sample mean.

Table 2. Variables Used In Regression Analyses

<u>Variable Number</u>	<u>Variable</u>
1	Occupational Exposure to Lead ^{1,2}
2	Years Smoked ¹
3	Frequency Smoked (Packs/Day) ¹
4	Pack-Years Smoked (Frequency Smoked × Years Smoked)
5	Years Since Cessation of Smoking ¹
6	Ex-Smoker ²
7	Non-Smoker ²
8	Age (Years) ¹
9	Age ² (Years ²)
10	Age ^{1/2} (Years ^{1/2})
11	Birth Year Post 1920 ¹
12	Years Since Retirement ¹
13	Death Before 25 Years of Age ^{1,2,3}
14	Ash Weight of Section B Rib ⁴
15	Death Due to Cancer ^{1,2}
16	Death Due to Cardiovascular Disease ^{1,2}
17	Presence of Nephrosclerosis at Death ^{1,2}
18	Ash as a Fraction of Wet Weight, Section B Rib ⁴
19	Male ^{1,2}

¹Relevant information was obtained from death certificates and/or hospital information.

²Variable coded as 1 if trait was present, and as 0 otherwise.

³Male and female non-smoking subgroups were the only groups with non-zero values for this variable.

⁴Section B rib represents a 3 cm section of rib, and was obtained as described in Esterby, 1976.

Table 3. Variables Excluded from Regressions for Donor Subgroups

Subgroup	Variables Excluded ^{1,2}
Male Non-Smokers	2,3,4,5,6,7,19
Female Non-Smokers	1,2,3,4,5,6,7,19
Male Smokers	6,7,13,19
Female Smokers	1,6,7,12,13,15,19
Male Ex-Smokers	6,7,13,15,16,19

¹Because the subgroups were formed on the basis of donor sex and smoking habit, variables 6, 7 and 19 could not be included in any subgroup.

²Variable numbers are defined in Table 2.

Table 4. C_p Analysis of Transformed and Untransformed Data

Transformed Data			Untransformed Data		
C_p	$(E(C_p))$	Model	C_p	$(E(C_p))$	Model
9.84	(9)	1,3,6,7,8, 9,14,18	7.45	(7)	1,4,10,14,15,18
10.04	(10)	1,2,4,6,7,8, 9,14,18	7.50	(8)	1,4,10,11,14, 15,18
9.83	(11)	1,2,4,6,7,8, 9,14,18,19 *	7.50	(8)	1,6,10,11,14, 15,18
10.37	(12)	1,2,4,6,7,8, 9,14,15,18,19	7.09	(9)	1,4,6,10,11, 14,15,18 *
10.07	(13)	1,2,4,6,7,8, 9,14,15,16,18,19	7.39	(10)	1,4,6,8,9,11 14,15,18

* Final regression model.

Table 5. Final Models for Transformed and Untransformed Data

Variable Number	Variable	Coefficient	Standard Error	T-Statistic	Significance Level
Transformed Data					
1	Occupation	.471	.100	4.68	~0.
2	Years Smoked	-.00847	.00378	-2.24	.026
4	Pack-Years Smoked	.00347	.00132	2.64	.009
6	Ex-Smoker	-.175	.0854	-2.05	.042
7	Non-Smoker	-.449	.129	-3.48	.001
8	Age ₂	.0594	.00874	6.79	~0.
9	Age	-.000382	.0000804	-4.75	~0.
14	Ash Weight	.280	.139	2.01	.045
18	Ash as a Fraction of Wet Weight	-1.35	.430	-3.14	.002
19	Male	.105	.0686	1.52	.129
Untransformed Data					
1	Occupation	16.6	2.86	5.80	~0.
4	Pack-Years Smoked	.151	.0229	6.59	~0.
6	Ex-Smoker	-3.62	2.32	-1.56	.121
10	Age ₂	2.28	1.02	2.23	.027
11	Birth Year Post 1920	-3.44	2.15	-1.59	.112
14	Ash Weight	9.76	3.51	2.78	.006
15	Cancer Death	4.79	3.05	1.57	.118
18	Ash as a Fraction of Wet Weight	-39.41	11.55	-3.41	.001

Table 6. Summary of Regression Models for Various Subgroups of the Study Population (Untransformed Data)

VARIABLE (NUMBER)	M A L E				F E M A L E			
	SMOKERS		EX-SMOKERS		NON-SMOKERS		SMOKERS	
	Coefficient (Standard Error)	Accumulated R ² (Order of Entry)	Coefficient (Standard Error)	Accumulated R ² (Order of Entry)	Coefficient (Standard Error)	Accumulated R ² (Order of Entry)	Coefficient (Standard Error)	Accumulated R ² (Order of Entry)
CONSTANT	53.30 (10.65)		19.76 (6.42)		140.5 (75.2)		221.51 (106.43)	2.38 (13.09)
OCCUPATIONAL EXPOSURE TO LEAD (1)	13.72 (4.05)	.28 (2)	10.75 (3.37)	.50 (2)	42.06 (6.90)	.40 (1)	*	*
YEARS SMOKED (2)					*		-.48 (.15)	.81 (4)
FREQUENCY SMOKED (PACKS/DAY) (3)	-13.18 (5.08)	.39 (4)			*			*
PACK-YEARS SMOKED (4)	.51 (.13)	.21 (1)	.20 (.068)	.28 (1)	*		-.10 (.06)	.83 (5)
YEARS SINCE CESSATION OF SMOKING (5)	*				*		*	*
AGE (YEARS) (8)					9.46 (4.4)	.62 (4)	13.23 (5.79)	.77 (2)
AGE ² (YEARS) ² (9)	-.0050 (.002)	.44 (6)	.0033 (.0012)	.70 (5)	-.04 (.02)	.67 (5)	-.064 (.023)	.71 (2)
(AGE) ^{1/2} (YEARS) ^{1/2} (10)					-72.58 (36.40)	.61 (2)	-95.4 (47.7)	.87 (1)
BIRTH YEAR POST 1920 (11)	-6.27 (4.05)	.46 (7)					-23.4 (3.6)	.70 (1)
YEARS SINCE RETIREMENT (12)							*	1.60 (.45)
DEATH BEFORE 25 YEARS OF AGE (13)	*		*				*	
ASH WEIGHT SECTION B RIB (14)			13.00 (5.61)	.65 (4)	11.95 (8.7)	.62 (3)		15.41 (7.92)
DEATH DUE TO CANCER (15)	28.83 (6.93)	.35 (3)	*				*	
DEATH DUE TO CARDIO- VASCULAR DISEASE (16)			*				4.91 (2.43)	.84 (6)
RESENCE OF NEPHROSCLEROSIS (17)			-7.24 (3.23)	.77 (6)				5.81 (2.87)
ASH AS A FRACTION OF WET WEIGHT (18)	-56.73 (23.91)	.42 (5)	-80.51 (22.24)	.60 (3)				-61.40 (24.03)

* Variable not considered in that subgroup.

Table 7. Predicted Values and 95% Confidence Intervals for a Single Future Observation for Individuals with Various Donor Characteristics

MALE							FEMALE			
Packs Per Day Smoked	Not Occupationally Exposed			Occupationally Exposed			Packs Per Day Smoked	Not Occupationally Exposed		
	Age	Pred. Mean	Conf. Int.	Age	Pred. Mean	Conf. Int.		Age	Pred. Mean	Conf. Int.
0 (Non- Smoker)	17	11.36	5.35- 24.11	17	18.19	8.40- 39.38	0 (Non- Smoker)	17	10.23	4.77- 21.91
	40	22.21	10.48- 47.05	40	35.57	16.46- 76.88		40	20.00	9.36- 42.72
	50	26.21	12.20- 56.30	50	41.97	19.16- 91.95		50	23.59	10.89- 51.14
	60	28.65	13.10- 62.66	60	45.88	20.58- 102.29		60	25.79	11.67- 56.99
	70	29.02	12.96- 64.98	70	46.47	20.38- 105.99		70	26.12	11.53- 59.20
	80	27.22	11.75- 63.09	80	43.60	18.49- 102.80		80	24.51	10.43- 57.60
0.5	17	17.86	8.45- 37.72	17	28.60	13.23- 61.83	0.5	17	16.08	7.58- 34.12
	40	36.34	17.72- 74.52	40	58.20	27.72- 122.22		40	32.71	15.89- 67.37
	50	43.63	21.27- 89.51	50	69.89	33.37- 146.77		50	39.28	19.05- 81.00
	60	48.53	23.56- 99.97	60	77.73	36.88- 163.82		60	43.69	21.07- 90.61
	70	50.01	24.05- 104.01	70	80.10	37.67- 170.30		70	45.03	21.46- 94.49
	80	47.75	22.48- 101.41	80	76.47	35.27- 165.82		80	42.99	20.02- 92.37
1.5	17	17.98	8.51- 37.99	17	28.80	13.32- 62.25	1.5	17	16.19	7.63- 34.35
	40	39.63	19.37- 81.08	40	63.48	30.34- 132.80		40	35.68	17.36- 73.35
	50	49.26	24.12- 100.64	50	78.90	37.81- 164.67		50	44.35	21.58- 91.16
	60	56.73	27.73- 116.06	60	90.86	43.52- 189.71		60	51.08	24.77- 105.33
	70	60.53	29.39- 124.66	70	96.94	46.19- 203.47		70	54.49	26.18- 113.42
	80	59.83	28.53- 125.44	80	95.82	44.92- 204.38		80	53.86	25.34- 114.48
2.5	17	18.11	8.57- 38.25	17	29.00	13.42- 62.68	2.5	17	16.30	7.68- 34.60
	40	43.22	21.05- 88.74	40	69.23	33.03- 145.10		40	38.92	18.85- 80.33
	50	55.63	27.04- 114.43	50	89.09	42.49- 186.80		50	50.08	24.18- 103.74
	60	66.32	32.04- 137.28	60	106.22	50.43- 223.71		60	59.71	28.58- 124.73
	70	73.26	34.95- 153.56	70	117.33	55.12- 249.71		70	65.96	31.09- 139.89
	80	74.96	34.89- 161.06	80	120.06	55.17- 261.30		80	67.49	30.95- 147.17

FISH POPULATIONS IN THE CALIBRATED
WATERSHEDS OF MUSKOKA-HALIBURTON

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Abstract

Twenty-four lakes in the Muskoka-Haliburton area of Ontario were chosen for study as to kinds and abundance of fishes. These lakes comprised the calibrated watersheds, calculated watersheds, and potential calibrated watersheds of the Ontario Ministry of Environment. In lakes Red Chalk, Crosson, Harp and Plastic, actual fish populations were determined by mark-recapture, and for the remaining lakes, relative abundance was estimated from catch and effort. Various aspects of these fish populations were investigated, including: zoogeography, community structure, species diversity, species frequency, age-class composition, growth, relative condition and others. The results are discussed in relation to similar analyses elsewhere, and in relation to the possible acidification of surface waters in the Muskoka-Haliburton region of Ontario.

Introduction

The purposes of this investigation were to:

- (i) Determine the kinds and abundance of fishes in a designated set of lakes in the Muskoka-Haliburton area of Ontario, in order to make possible comparisons in the future, and to relate such changes to acid loading and other environmental variables.
- (ii) Examine the attributes of the current populations for evidence of acid stress.
- (iii) Determine the mechanisms of action of acid stress, where such were found, under field and laboratory conditions.

The lake set chosen by the Ontario Ministry of Environment was composed primarily of the lakes of the earlier Lakeshore Capacity Study, for which considerable data was available already. To this L.C.S. set were added a few lakes of low alkalinity in order to expand the range of water chemistry to near zero alkalinity. The lakes are identified as to latitude and longitude (Table 1). These lakes are portions of four drainage systems (Fig. 1). Lakes Chub, Dickie, Bigwind, Leech, Heeney, Healey, McKay, Moot and Buck drain into the South Muskoka River. Lakes Solitaire, Little Clear, Fawn, Harp and Walker drain into the North Muskoka River. The North and South Muskoka rivers enter Muskoka Lake into which Leonard Lake also drains, and thence into Georgian Bay via Go Home Lake or the Moon River. Lakes Plastic, Clear, Basshaunt and Glen drain into the Gull River, thence via the Trent Canal System into Lake Ontario. Lakes Gullfeather, Poker, Cinder, Crosson, Red Chalk flow into the Black River, thence via the Severn River into Georgian Bay. Thus, fish access to the study lakes has been from both Lake Huron and Lake Ontario.

Table 1. Lake identification for the 24 study lakes of the Muskoka-Haliburton region.

		TOWNSHIP	LAT & LONG ° °		AREA (ha)	pH
I	Relative Abundance Lakes					
Chub	Ridout	45 13	78 59	32.3	5.91	
Clear	Sherbourne	45 11	78 43	38.4	6.57	
Dickie	McLean	45 09	79 05	93.2	5.75	
Walker	Sinclair	45 23	79 05	68.2	7.25	
Little Clear	Sinclair	45 25	79 00	10.9	6.84	
Buck	Sinclair	45 23	79 00	40.3	6.33	
Solitaire	Sinclair	45 23	79 01	122.4	6.89	
Bigwind	Oakley	45 03	79 03	106.5	6.76	
Gullfeather	Oakley	45 06	79 01	65.9	5.89	
Basshaunt	Guildford	45 07	78 08	47.3	6.72	
Glen	Guildford	45 08	78 09	16.3	8.38	
Heeney	McLean	45 08	79 06	21.5	5.74	
Fawn	Macaulay + Stephen	45 10	79 15	36.6	5.56	
Leech	Oakley	45 03	79 06	82.0	6.99	
McKay	Draper	45 03	79 10	138.3	6.18	
Healey	Macaulay	45 05	79 11	119.0	6.14	
Moot	McLean	45 03	79 10	46.2	6.10	
Cinder	Hindon	45 04	78 56	39.7	6.62	
Poker	Hindon	45 03	78 56	21.0	6.72	
Leonard	Monck	45 04	79 27	137.0	6.96	
II	Population Estimate Lakes					
Red Chalk	Ridout	45 11	78 57	56.9	6.30	
Harp	Chaffey	45 23	79 07	66.9	6.30	
Crosson	Oakley	45 05	79 02	56.8	5.30	
Plastic	Sherbourne	45 11	78 50	32.6	5.20	

Fig. 1. Map of the Muskoka-Haliburton region, with the location of the twenty-four study lakes.



The Muskoka-Haliburton lakes could not be viewed in isolation as to evidence of environmental stress, especially with respect to population perturbations. The approach throughout much of this report is thus comparative, with the principle comparisons drawn with other acidified lakes in Ontario, such as those of La Cloche and Wawa, and non-acidified areas, such as Manitoulin and Bruce. International comparisons were made in two recent reviews (Harvey and Lee, 1981; Harvey, 1981) and are not repeated in this report.

Fish populations show a limited variety of responses to environmental stresses. For example, populations may become larger or smaller, grow more quickly or more slowly, change in age-class composition, mature at an earlier age or later. To date, no 'unique' response has been found to occur in fish populations experiencing acid stress. One of the most common population changes in acidifying lakes is the failure of recruitment of a new year-class into the population. This has been identified for example in bass and perch populations in response to low temperatures at spawning. Thus, while population studies can be used legitimately as the early warning of the untoward effects of acidification, such studies alone cannot ascribe causality. Population studies of the type reported here are essential also to establish the magnitude of any response to acid stress. It was for this reason that the sample was expanded to twenty-four lakes spanning a wide range of pH and alkalinity.

In contrast to the general nature of population responses to acid stress, individual fish respond much more precisely. For example, aluminum liberated from soils by acid precipitation accumulates in mucus on fish gills. Distress and death occur at predictable, reproducible concentrations of aluminum on the gills. Similarly, the failure of age-class recruitment can

be traced to individual fish failing to mature, possibly to failed spawning, or to the death of larvae on hatching. The loss of older age-classes from populations may be due to loss of body calcium or to the accumulation of manganese in bony tissue. Studies on these mechanisms of action were conducted concurrently with the population work, and have been reported separately elsewhere (Fraser and Harvey, 1981; Harvey, Fraser and Lee, 1982; Harvey, Dillon, Fraser, Somers, Fraser and Lee, 1982; and in several M.Sc. theses).

Table 2. The numbers of fish sampled by species and lake.

SPECIES	CHUB	CLEAR	DICKIE	WALKER	LITTLE CLEAR	BUCK	SOLITAIRE	BIGMIND	GULLFEATHER	BASSHAUNT	GLEN	HEENEY	FAWN	LEECH	McKAY	HEALEY	MOOT	CINDER	POKER	LEONARD	NO. OF LAKES
Rainbow trout	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3	3
Brook trout	-	-	-	-	3	-	2	4	-	-	-	-	-	-	-	-	-	-	-	-	3
Lake trout	4	-	-	2	2	17	-	3	9	-	-	-	-	-	-	-	-	-	-	-	6
Lake whitefish	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	40	1
Round whitefish	-	-	-	-	-	-	25	-	-	-	-	-	-	-	-	-	-	-	-	-	1
White sucker	-	68	140	-	12	69	86	88	108	-	15	21	108	24	109	8	48	68	36	1	17
N. Redbelly dace	100	-	3	-	16	-	-	7	-	-	-	-	49	-	-	-	-	2	16	-	7
Lake Chub	-	-	-	-	-	-	5	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Brassy minnow	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2	-	-	1
Golden shiner	-	-	20	44	1	-	-	21	37	-	1	-	15	-	2	7	14	55	-	6	12
Common shiner	-	-	-	-	51	-	22	-	-	-	-	-	56	-	-	1	-	-	-	-	4
Blacknose shiner	-	-	-	-	-	-	-	-	2	-	-	9	-	-	-	-	-	-	2	-	3
Bluntnose minnow	-	-	-	-	-	-	-	136	-	-	-	-	-	-	-	-	-	-	-	-	1
Fathead minnow	-	-	-	-	-	-	1	7	-	-	-	-	-	-	-	-	-	-	-	-	2
Creek chub	145	-	5	-	32	1	49	-	1	11	-	5	1	-	-	20	-	40	28	-	12
Pearl dace	-	-	4	-	5	-	-	-	-	-	-	-	1	-	-	-	-	-	2	-	4
Brown bullhead	-	4	108	-	2	-	30	38	-	18	-	125	79	4	4	51	58	-	36	64	13
Burbot	-	-	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
Brook stickleback	-	-	-	-	-	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Trout perch	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Rock bass	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	-	1
Pumpkinseed	-	52	52	120	12	-	-	-	-	207	207	-	-	67	42	-	-	-	-	99	4
Smallmouth bass	-	26	-	52	2	55	14	127	93	202	76	153	50	130	85	105	19	101	137	159	17
Largemouth bass	-	2	24	-	2	-	-	-	17	26	2	6	1	7	23	8	-	-	-	4	13
Yellow perch	11	87	5	103	145	3	149	198	59	-	16	123	112	14	20	24	4	105	108	123	19
Iowa darter	-	-	-	1	3	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	7
Mottled sculpin	-	-	-	-	-	-	-	-	-	-	3	-	-	-	-	-	-	-	-	-	3
N. redbelly	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
dace hybrid	-	-	-	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
TOTAL NO. SPECIES	4	7	9	6	15	6	11	10	7	5	7	7	12	7	8	8	6	7	8	9	-
TOTAL NO. FISH SAMPLED	260	-	361	-	304	-	383	-	317	-	320	-	525	-	301	-	277	-	365	-	-
	-	240	-	332	-	157	-	630	-	266	-	442	-	552	-	224	-	373	-	499	-

Methodology

Relative abundance of fishes was determined by sampling each lake with a standard set of sampling gear: experimental gill nets, coarse mesh and fine-mesh trap nets, transparent plastic traps, and baited minnow traps. Sampling was conducted within all habitats to maximize the likelihood of capturing all fish species present. Sampling effort was similar between the 20 lakes during 1979-80.

The actual number of fish sampled was less than the number caught, where capture exceeded 100. Thus data on weight, length, sex, and maturity, was recorded only for the numbers of fishes identified in Table 2.

Absolute population estimates were made for four lakes: Red Chalk, Harp, Crosson and Plastic, based on the principle of mark and recapture. Marking was primarily by tagging, with a total of 11,377 marks applied 1979-80. Spaghetti tags were attached under the base of the dorsal fin to fish above a minimum size, specifically: white sucker 15 cm, common shiner 15 cm, creek chub 15 cm, brown bullhead 13 cm, burbot 20 cm, pumpkinseed 10 cm, smallmouth bass 15 cm, yellow perch 15 cm. Fish smaller than this were marked by fin-clip, with the left pelvic fin clipped during the marking in the summer of 1979 and the spring of 1980, and the right pelvic clipped during the fall recapture of 1979. In general, four weeks of fish tagging were required on each lake, May-August, 1979. Recapture was attempted in the fall of 1979 and again in the spring of 1980, each lake requiring two weeks. Both tagging and recapture effort were dependent on population size. For example, a species population of 1,600 fish would require 25% of the animals to be tagged, and a recovery of 25% of the marked fish for the population estimate to be within 10% of the actual population with 95% probability, based on the nomogram of

Robson and Regier (1964).

Field measurements on fish included weight, length, sex, state of maturation, plus samples of scales, fin-rays, bones, or otoliths, depending on the species sampled.

Physical and chemical data on the 24 study lakes was supplied by the Ontario Ministry of Environment, and supplemented by additional data on lakes Crosson, Solitaire, and Plastic from the Lake Ecosystem Working Group.

Data analysis was directed at several aspects:

Absolute fish populations were calculated as Peterson estimates for twenty species populations in four lakes.

Biomass was calculated for the three white sucker populations estimated by mark-recapture, and related to lake pH and previous measures of the density of this species.

Relative abundance of fishes was estimated for twenty lakes, based on the most abundant species in each lake scaled to 100 and other species scaled in proportion, for comparison within lakes.

Species diversity was calculated according to Shannon-Weaver's index of diversity, $-\sum p_i \times \log_e p_i$ using the scaled abundance estimates.

Growth and age-class composition of selected species was plotted and related to environmental variables. The condition factor of white suckers was calculated as $CF = W/L^3$

Simple correlations were calculated for the number of species in relation to environmental and morphometric variables, especially pH and lake size. Frequency of occurrence of fish species was compared between the Muskoka-Haliburton lakes and other lake sets.

Community structure was determined by unweighted-pair cluster analysis, using the Jaccard coefficient of similarity on fish presence/absence. The communities so identified were compared with those found in other Ontario lake sets.

Definition of Lake pH

As one objective of this study was to relate the status of lake biota to acidity, it was necessary to define lake pH. The difficulty of doing this from a single measurement at any depth is apparent from Figures 2 and 3. Crosson Lake (Fig. 2) showed a progressive increase in the pH of epilimnial waters as warming took place, with pH remaining unchanged below the thermocline. In contrast, Solitaire L. (Fig. 3) showed a pronounced positive heterograde curve with the thermocline exceeding the pH of the hypolimnion by as much as 2.5 pH units. Plastic L. (Fig. 3) was representative of a third pattern, with small increases in pH of surface meta- and hypolimnetic waters during the summer. The pH values used for this study were supplied by the O.M.E. and are presented in Table 1. The sampling period was late May to early June, 1980, with volume weighted pH values being used for Lakes Red Chalk, Harp, Crosson and Plastic.

Fig. 2. Principle chemical and physical features of Crosson Lake, measured vertically at eight times, 1979. Courtesy: Lake Ecosystem Working Group.

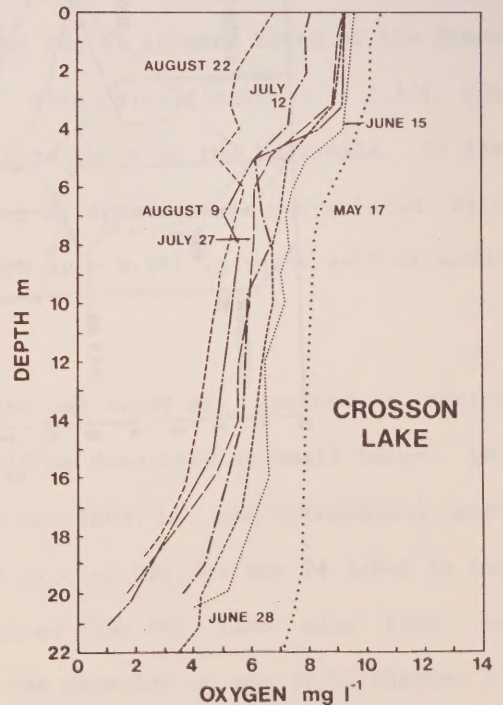
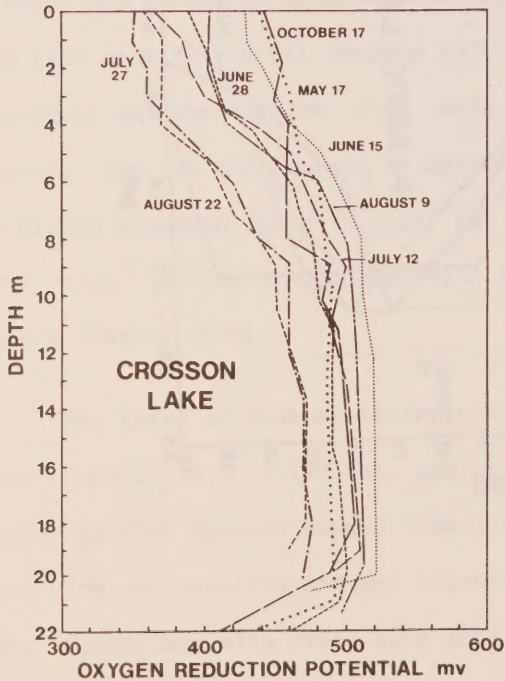
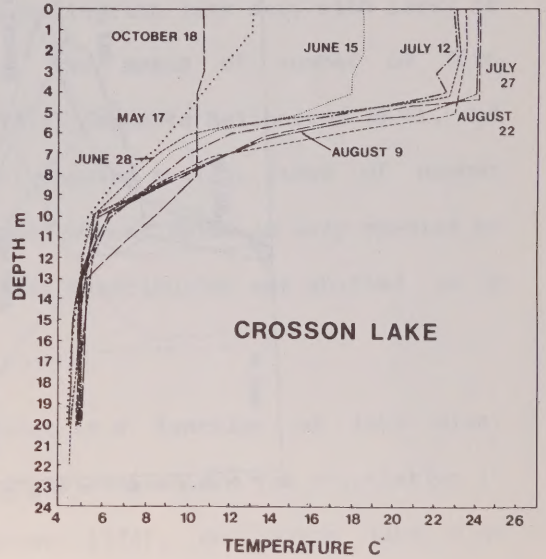
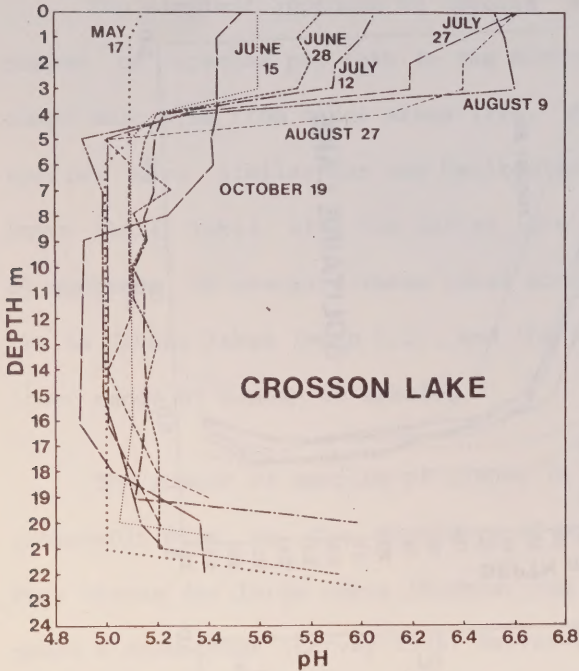
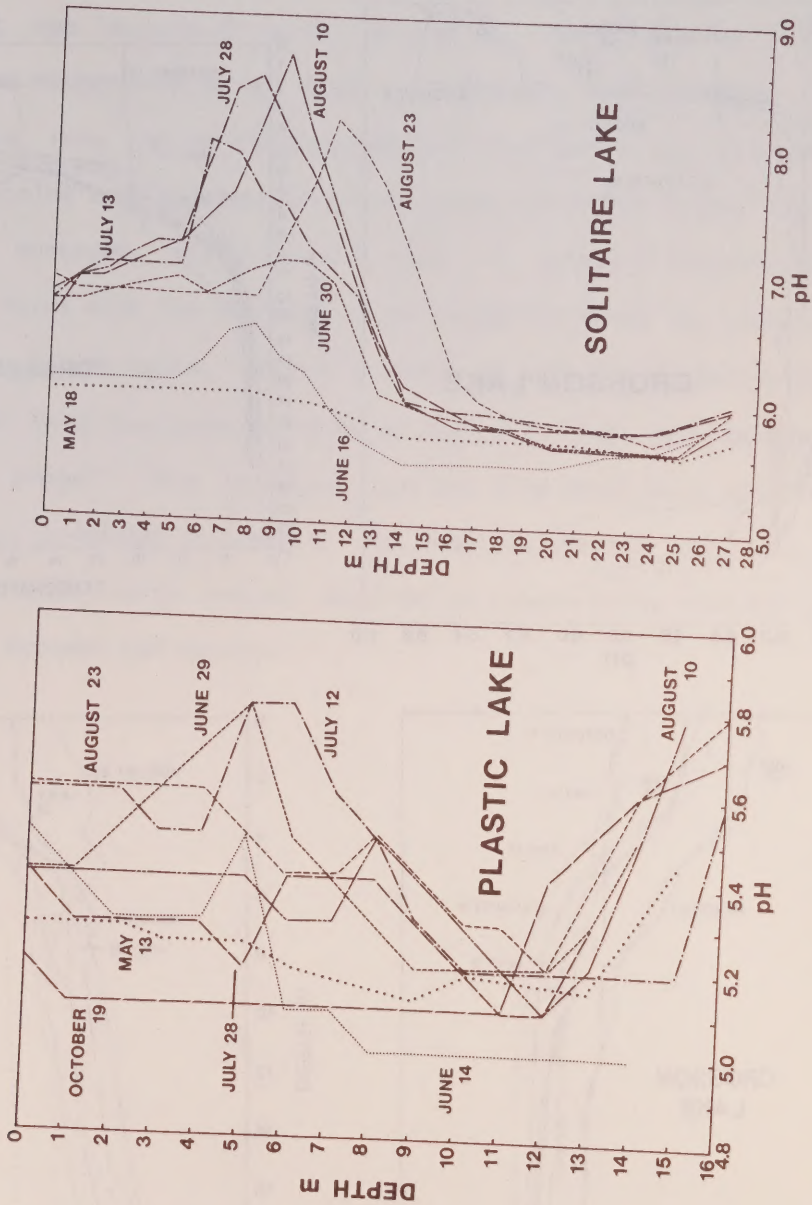


Fig. 3. Vertical pH of lakes Plastic and Solitaire, 1979. Courtesy: Lake Ecosystem Working Group.



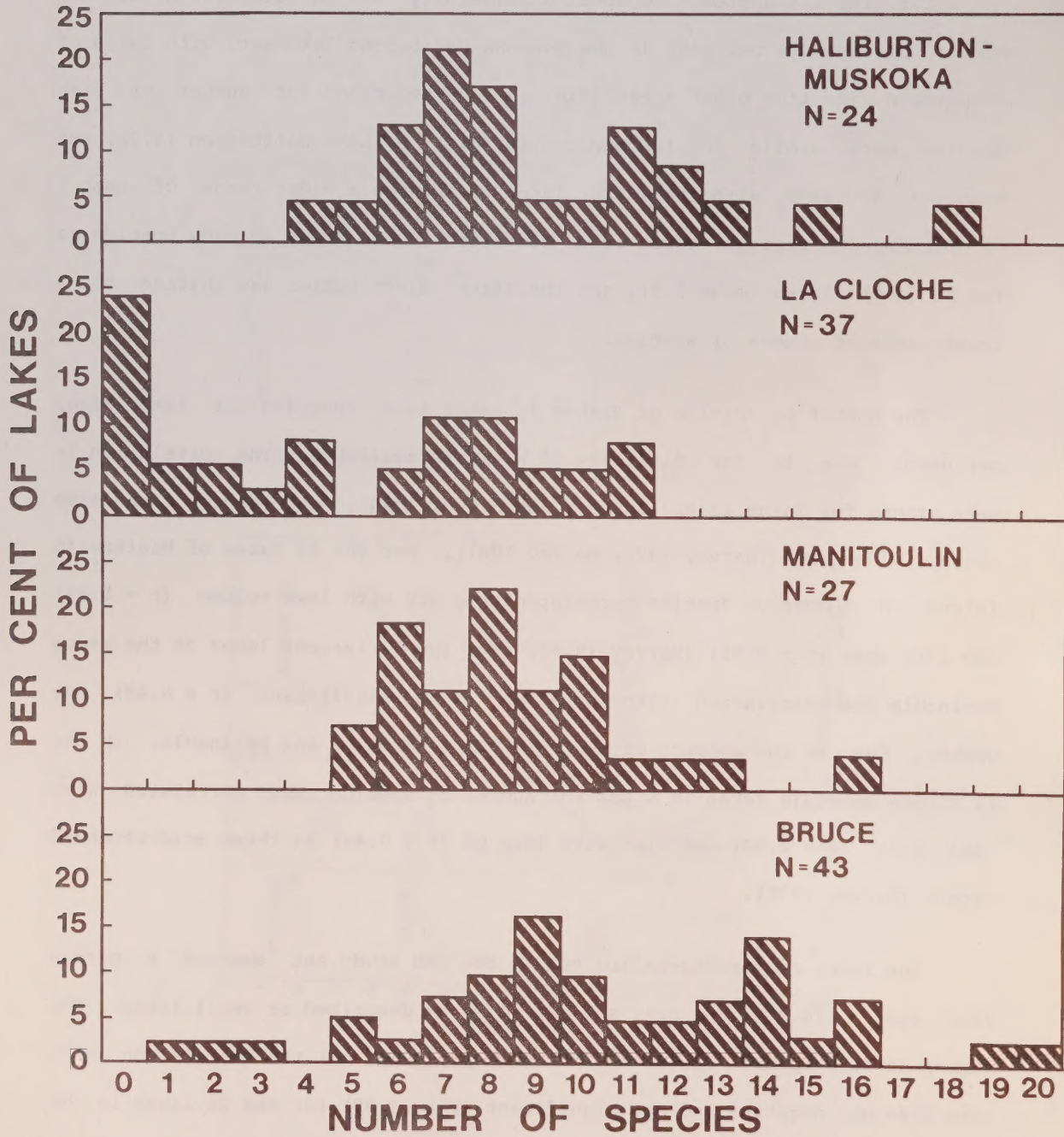
Number of Fish Species

The simplest approach to species diversity was a comparison of the number of species per lake in the Muskoka-Haliburton lake set, with lakes of comparable size from other areas (Fig. 4). The means of number of fish species were similar for the Manitoulin (8.4), Muskoka-Haliburton (9.0), and Bruce (10.4) lakes, with the latter lake set showing a wider range of number of species. On average, these lakes contained almost twice as many species as the La Cloche lakes (mean 5.2), and the latter distribution was shifted to a lower range of number of species.

The number of species of fishes in lakes is a function of lake size, presumably due to the diversity of habitats available. The correlation is very strong for large lakes (Barbour and Brown, 1974), and where lake size spans a wide range (Harvey 1978; Harvey 1981). For the 52 lakes of Manitoulin Island, the number of species correlated strongly with lake volume ($r = 0.84$) and lake area ($r = 0.81$) (Harvey 1978). For the 57 largest lakes of the Bruce Peninsula the correlation with area was also significant ($r = 0.48$) but weaker, due to the absence of any very large lakes on the Peninsula. In the La Cloche Mountain lakes ($n = 68$) the number of species was correlated with lake size ($r = 0.59$) and also with lake pH ($r = 0.46$) in these acid-stressed waters (Harvey 1975).

The lakes of Muskoka-Haliburton in the OME study set spanned a narrow size range (10.9 - 187 ha), and all would be described as small lakes. The number of fish species ranged from 4 to 18 per lake, but the correlation with lake size was negative and not significant ($r = -0.09$) for the 24 lakes in the set. Comparison with other lake sets required that the lake size range be comparable. Accordingly, the analysis was repeated on the 37 La Cloche, 27

Fig. 4. Frequency distribution of lakes, based on the number of fish species present, for four regions of Ontario.



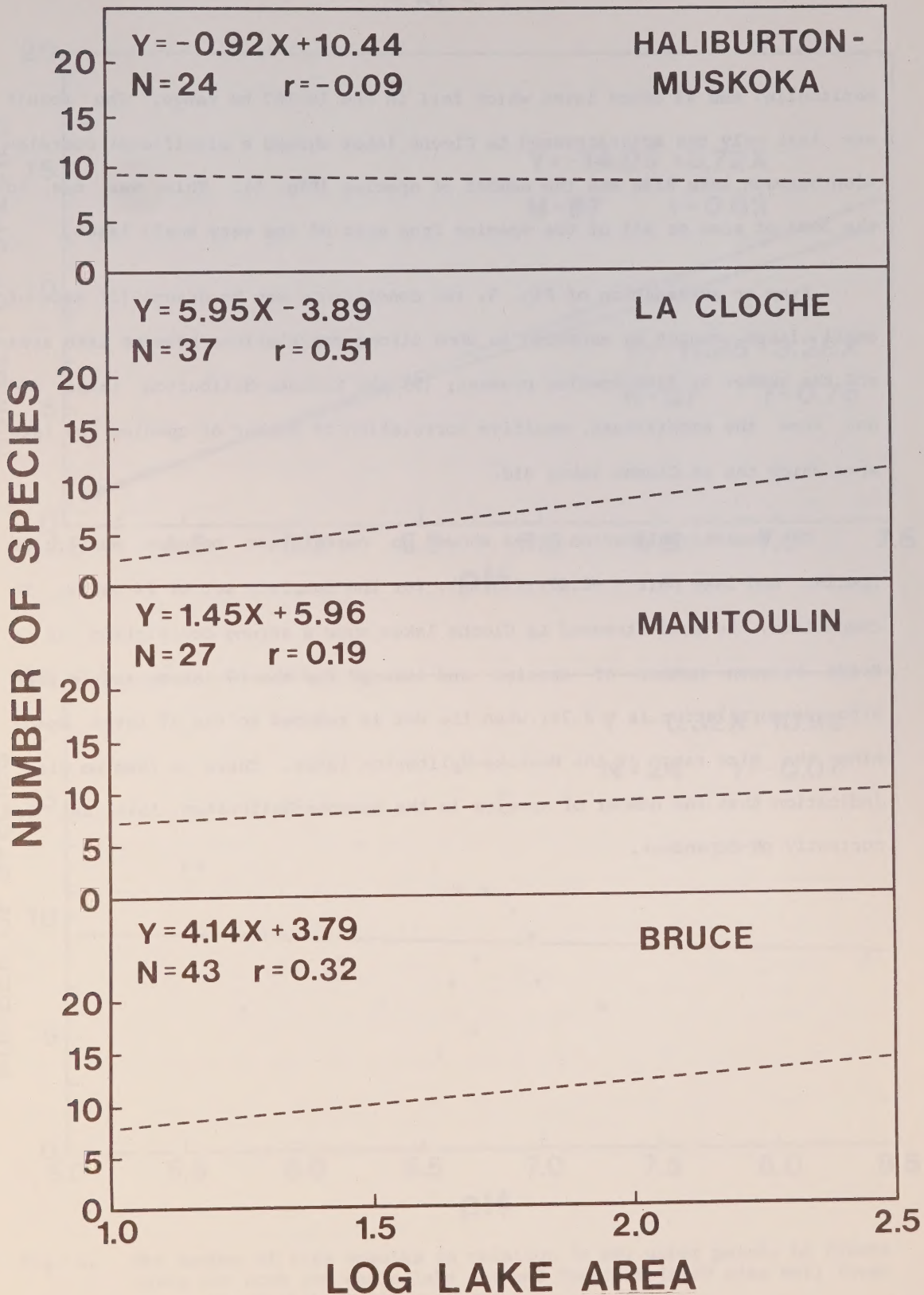


Fig. 5. The relationship between lake size and number of fish species, for lakes of comparable size from four regions in Ontario.

Manitoulin, and 43 Bruce lakes which fell in the 10-187 ha range. The result was that only the acid-stressed La Cloche lakes showed a significant correlation between lake size and the number of species (Fig. 5). This was due to the loss of some or all of the species from most of the very small lakes.

From an examination of Fig. 5, two conclusions may be drawn: (1) sets of small lakes cannot be expected to show strong correlations between lake area and the number of fish species present; (2) the Muskoka-Haliburton lakes did not show the significant, positive correlation of number of species and lake area which the La Cloche lakes did.

The Muskoka-Haliburton lakes showed no correlation between number of species and lake pH ($r = -0.67$) (Fig. 6), for the complete set of 24 lakes. In comparison, the acid-stressed La Cloche lakes show a strong correlation ($r = 0.63$) between number of species and lake pH for the 67 lakes, and an even stronger correlation ($r = 0.76$) when the set is reduced to the 37 lakes spanning the size range of the Muskoka-Haliburton lakes. There is thus no clear indication that the number of species in the Muskoka-Haliburton lake set is currently pH-dependent.

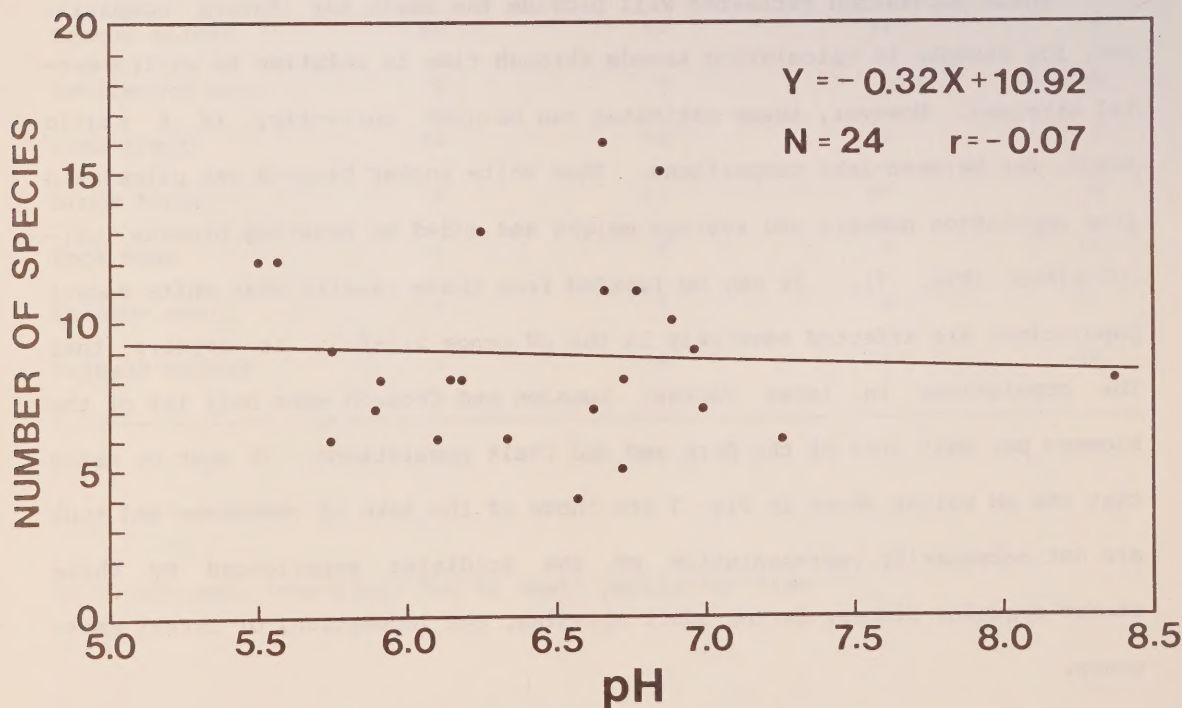
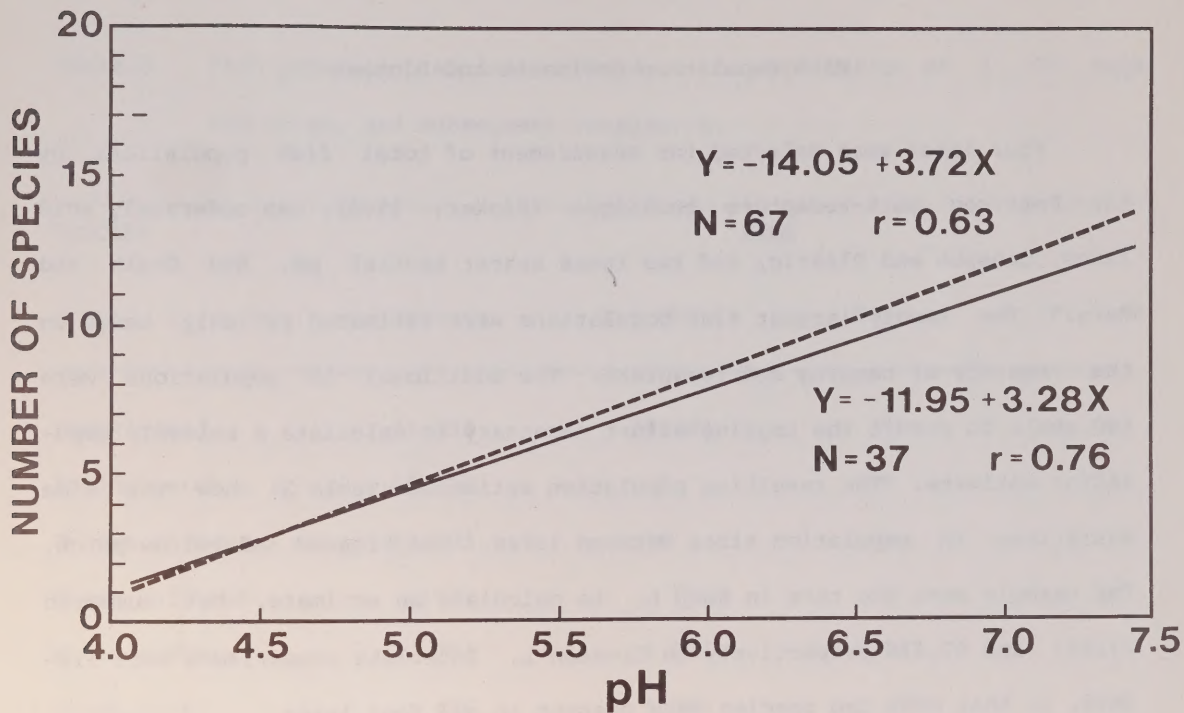


Fig. 6. The number of fish species in relation to pH: upper panel, La Cloche lakes for both the whole lake set and the restricted size set; lower panel, the Muskoka-Haliburton set.

Fish Population Estimates and Biomass

Four lakes were selected for measurement of total fish populations by the Petersen mark-recapture technique (Ricker, 1968): two moderately acid lakes, Crosson and Plastic, and two lakes nearer neutral pH, Red Chalk and Harp. The twenty largest fish populations were estimated reliably, based on the frequency of tagging and recapture. The additional 15 populations were too small to permit the tagging effort necessary to calculate a reliable population estimate. The resulting population estimates (Table 3) show the wide variations in population sizes between lakes. Pumpkinseed and yellow perch, for example were too rare in Harp L. to calculate an estimate, but numbered 47,353 and 67,136 respectively in Crosson L. Interlake comparisons were limited, in that only two species were present in all four lakes.

These population estimates will provide the basis for future comparisons, for example in calculating trends through time in relation to environmental stresses. However, these estimates can be used currently, in a static sense, for between-lake comparisons. Thus white sucker biomass was calculated from population numbers and average weight and added to existing biomass calculations (Fig. 7). It may be implied from these results that white sucker populations are affected adversely in the pH range 5.7-6.3. It appears that the populations in lakes George, Lumsden and Crosson were only 10% of the biomass per unit area of the Harp and Red Chalk populations. It must be noted that the pH values shown in Fig. 7 are those of the lake of residence and thus are not necessarily representative of the acidities experienced by these stream-spawning fishes, during adult spawning, egg incubation, or larval emergence.

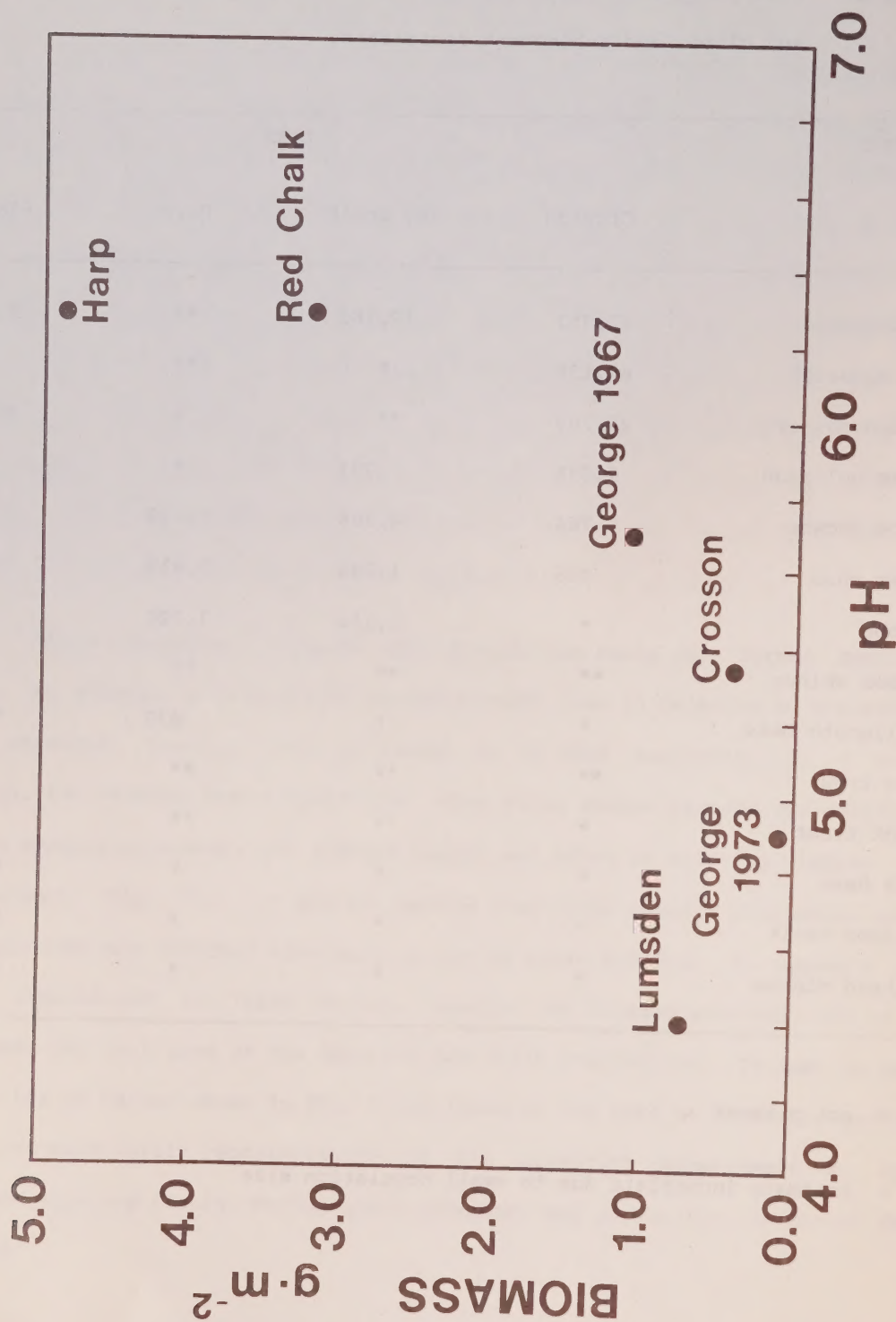
Table 3. Fish population estimates based on the application of 11,377 tags and clips, and subsequent recaptures.

SPECIES	LAKE			
	Crosson	Red Chalk	Harp	Plastic
Pumpkinseed	47,353	12,163	**	8,896
Yellow perch	67,136	*	**	203
Golden shiner	22,703	**	*	3,033
Brown bullhead	1,531	793	*	837
White sucker	764	4,206	7,003	*
Creek chub	406	1,286	2,419	810
Burbot	*	1,150	1,320	*
Common shiner	**	**	**	*
Smallmouth bass	*	*	832	**
Lake trout	**	**	**	*
Brook trout	*	**	**	*
Rock bass	*	*	*	**
Rainbow smelt	*	*	*	**
Fathead minnow	*	*	*	**

* = not present

** = estimate incomplete due to small population size

Fig. 7. Biomass estimates of white sucker in lakes over a range of pH.
Source: Lumsden Lake, Beamish, 1970; George Lake, Beamish et al., 1975.



Fish Relative Abundance

In the remaining 20 lakes, the standard sampling procedure yielded a variable number of each species (Table 4). Such numbers normally are divided by capture effort in order to facilitate comparison. In view of the similarity of effort, a first approximation of abundance can be had from simple comparison of catches. Thus it is likely that the yellow perch is about 100X more abundant in Clear L. than Dickie L. (Table 4).

The number of fish captured can be related to environmental variables, for example lake pH, for the more frequently occurring species. Where this was done, there was no significant correlation between pH and abundance of yellow perch, smallmouth bass, and pumpkinseed. White sucker abundance was correlated negatively with pH, possibly due to the absence of lakes in the set of pH lower than 5.6 (Fig. 8), the pH range where this species is susceptible.

The number of fish species was correlated strongly ($r = 0.73$) with species diversity, as measured by the Shannon-Weaver index. This implies that sampling was effective, in that a broad scatter of points would have resulted from improper sampling (Fig. 9). Three lakes fell in the low diversity range of 0-1: Basshaunt, Clear and Glen. Lakes Clear and Basshaunt were not very acid, and Glen L. had a pH of 8.3. However, Clear Lake is noteworthy in that this lake lost most of its bicarbonate alkalinity in recent years (Dillon, 1981). Only one lake fell in the high-diversity range 2-3, Fawn L. This distribution is in contrast to lake sets examined previously, in which diversities of unstressed lakes were higher (Harvey 1975, 1978) but with the reservation that abundance had not been scaled in the same manner in these previous studies. The value of this analysis was thus to draw attention to the low species diversity of this lake set in general and in particular to lakes Basshaunt, Clear and Glen.

Table 4. Total numbers of fish captured by species and lake.

SPECIES	CHUB	CLEAR	DICKIE	WALKER	LITTLE CLEAR	BUCK	SOLITAIRE	BIGWIND	GULLFEATHER	BASSHAUNT	GLEN	HEENEY	FAWN	LEECH	McKAY	HEALEY	MOOT	CINDER	POKER	LEONARD	NO. OF LAKES
Rainbow trout	1	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	3	3
Brook trout	-	-	-	-	3	-	2	4	-	-	-	-	-	-	-	-	-	-	-	-	3
Lake trout	-	4	-	2	2	17	-	3	-	10	-	-	-	-	-	-	-	-	-	-	3
Lake whitefish	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6
Round whitefish	-	-	-	-	-	-	25	-	-	-	-	-	-	-	-	-	-	-	-	40	1
White sucker	68	-	140	-	12	69	89	91	108	-	15	21	109	25	113	10	78	70	36	1	1
N. redbelly dace	-	16	3	-	56	-	-	7	-	-	-	-	49	-	-	-	-	4	16	-	17
Lake chub	-	-	-	-	-	-	6	-	-	-	-	-	-	-	-	-	-	-	-	7	7
Brassy minnow	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Golden shiner	3	-	20	44	1	-	-	26	37	-	1	-	15	-	2	8	14	2	-	-	1
Common shiner	-	-	-	-	57	-	27	-	2	-	-	-	56	-	-	1	-	77	-	6	13
Blacknose shiner	-	-	-	-	-	-	-	-	-	-	-	9	-	-	-	-	-	-	-	-	1
Bluntnose minnow	-	-	-	-	-	-	-	211	-	-	-	-	-	-	-	-	-	-	2	-	4
Fathead minnow	-	-	-	-	-	-	1	7	-	-	-	-	-	-	-	-	-	-	-	-	340
Creek chub	-	145	5	-	34	1	108	-	1	11	-	5	1	-	-	20	-	54	28	-	2
Pearl dace	-	-	4	-	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Brown bullhead	4	-	107	-	2	-	-	47	-	18	-	129	79	4	4	84	58	-	40	126	13
Burbot	-	-	-	-	15	-	30	-	-	-	-	-	-	-	-	-	-	-	-	-	4
Brook stickleback	-	-	-	-	-	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
Trout perch	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Rock bass	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	-	1
Pumpkinseed	54	-	72	342	12	-	-	-	-	337	337	-	-	68	42	-	-	-	-	-	1
Smallmouth bass	26	-	*	53	2	55	107	136	93	399	101	557	50	132	190	147	19	266	492	100	4
Largemouth bass	2	-	25	-	-	-	-	-	17	26	2	6	1	7	23	8	-	-	222	222	17
Yellow perch	87	489	5	128	204	3	482	262	134	-	16	182	52	6	16	-	4	-	-	4	13
Iowa darter	-	-	-	1	3	-	3	-	-	-	-	-	127	14	22	33	160	124	102	237	7
Mottled sculpin	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19	19
N. redbelly	-	-	-	-	-	-	-	-	-	-	3	-	-	-	-	-	-	-	-	-	3
dace hybrid	-	-	-	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
TOTAL NO. SPECIES	8	4	10	6	15	6	11	11	7	5	7	7	12	7	8	8	6	7	8	-	1
TOTAL NO. FISH	245	654	381	570	151	880	795	392	464	475	909	541	256	412	311	333	597	718	739	-	-

↓ Catch represented largely by young-of-the-year. See catch sheets.
* Present. Caught during subsequent sampling.

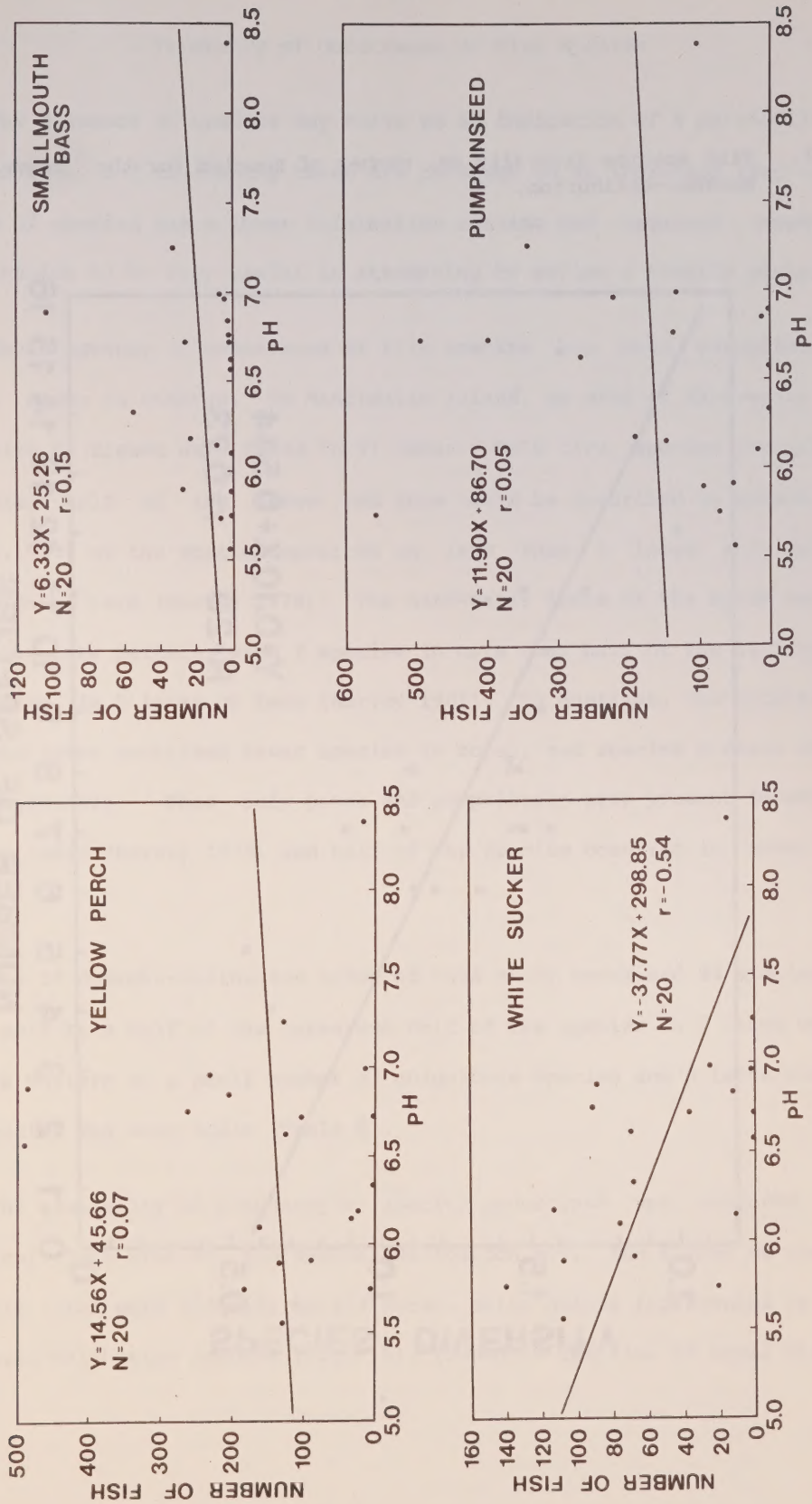
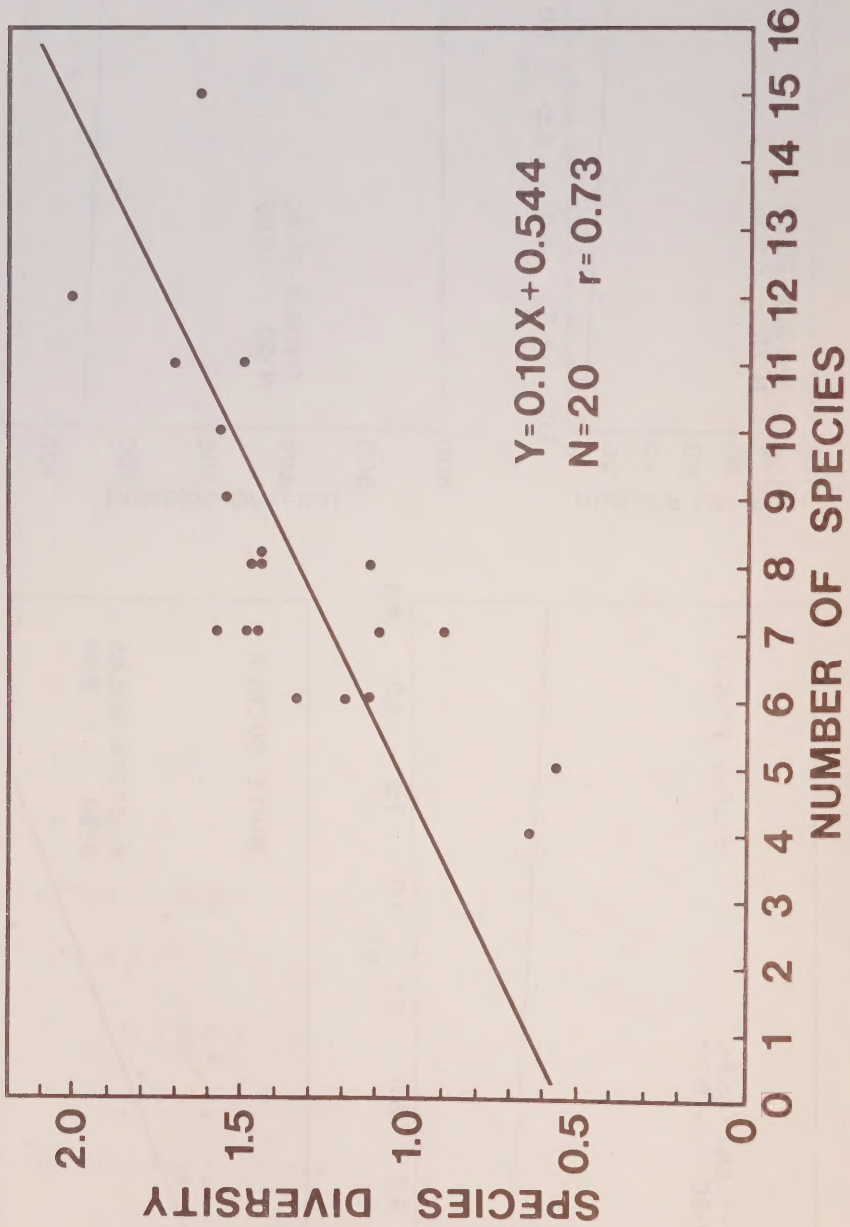


Fig. 8. Number of fish species vs. lake pH for the four most common fishes, in the twenty lake set.

Fig. 9. Fish species diversity vs. number of species for the twenty lakes, Muskoka-Haliburton.



Frequency of Occurrence of Fish Species

The presence of species may serve as an indication of a particular habitat condition, and frequently these are referred to as indicator species. The absence of species has a lower information content and requires experimental corroboration to be very useful in attempting to define a hostile environment.

The frequency of occurrence of fish species has been established for several areas in Ontario. On Manitoulin Island, an area of hard-water lakes, 43 species of fishes were found in 51 lakes. Only five species occurred in more than half of the lakes and thus could be described as common. Conversely, half of the species occurred in less than 5 lakes and could be described as rare (Harvey 1978). The hard-water lakes of the Bruce Peninsula showed the same pattern, with 7 species in more than half of the 57 lakes, and 22 species in 5 lakes or less (Harvey 1981). In contrast, the acid-stressed La Cloche lakes contained fewer species in total, and species present occurred less frequently. Thus only perch and pumpkinseed were present in more than half the lakes (Harvey 1975) and half of the species occurred in seven lakes or less.

The 24 Muskoka-Haliburton lakes of this study contained 34 species, with 7 in more than half of the lakes and half of the species in 3 lakes or less. Thus the pattern of a small number of ubiquitous species and a large number of rare species was seen again (Table 5).

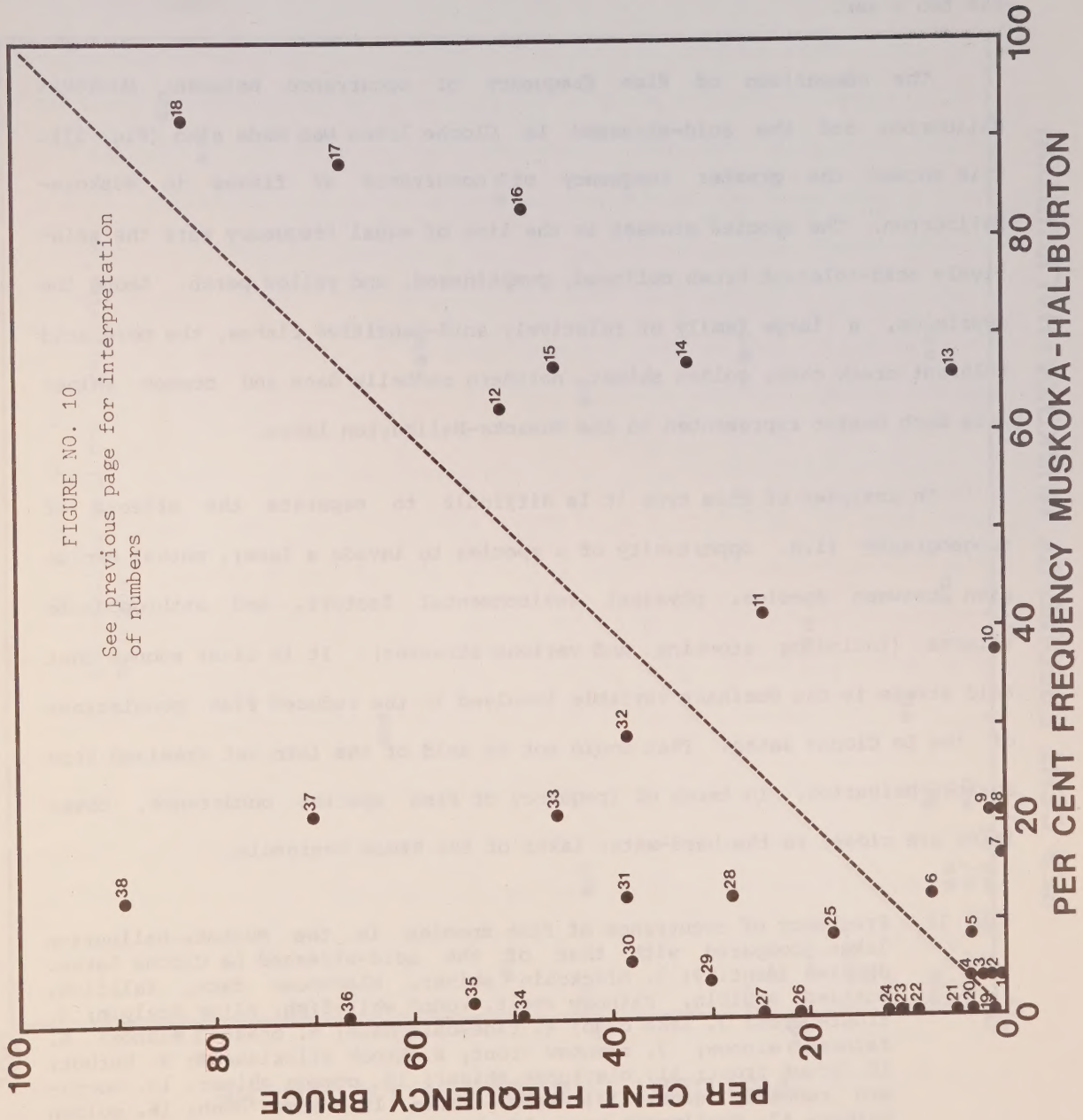
The similarity of frequency of species occurrence was compared for a hard-water lake area vs the Muskoka-Haliburton set. The fishes of the Bruce Peninsula lakes were slightly more diverse, being better represented by 20 vs 18 Muskoka-Haliburton species (Fig. 10), (based on the line of equal frequency

Table 5. Frequency of occurrence of fishes in the Muskoka-Haliburton lake set, N = 24.

Scientific name	Common name	Number of lakes	Per cent of lakes
<i>Perca flavescens</i>	Yellow perch	22	91.7
<i>Lepomis gibbosus</i>	Pumpkinseed	21	87.5
<i>Catostomus commersoni</i>	White sucker	20	83.3
<i>Ictalurus nebulosus</i>	Brown bullhead	16	66.7
<i>Notemigonus crysoleucas</i>	Golden shiner	16	66.7
<i>Semotilus atromaculatus</i>	Creek chub	16	66.7
<i>Micropterus dolomieu</i>	Smallmouth bass	15	62.5
<i>Chrosomus eos</i>	Northern redbelly dace	10	41.7
<i>Salvelinus namaycush</i>	Lake trout	9	37.5
<i>Micropterus salmoides</i>	Largemouth bass	8	33.3
<i>Notropis cornutus</i>	Common shiner	7	29.2
<i>Ambloplites rupestris</i>	Rock bass	5	20.8
<i>Notropis heterolepis</i>	Blacknose shiner	5	20.8
<i>Salvelinus fontinalis</i>	Brook trout	5	20.8
<i>Semotilus margarita</i>	Pearl dace	5	20.8
<i>Lota lota</i>	Burbot	4	16.7
<i>Etheostoma exile</i>	Iowa darter	3	12.5
<i>Culaea inconstans</i>	Brook stickleback	3	12.5
<i>Salmo gairdneri</i>	Rainbow trout	3	12.5
<i>Pimephales promelas</i>	Fathead minnow	3	12.5
<i>Hybognathus hankinsoni</i>	Brassy minnow	2	8.3
<i>Chrosomus neogaeus</i>	Finescale dace	2	8.3
<i>Coregonus artedii</i>	Lake herring	1	4.2
<i>Pimephales notatus</i>	Bluntnose minnow	1	4.2
<i>Coregonus clupeaformis</i>	Lake whitefish	1	4.2
<i>Couesius plumbeus</i>	Lake chub	1	4.2
<i>Percopsis omiscomaycus</i>	Trout-perch	1	4.2
<i>Cottus bairdi</i>	Mottled sculpin	1	4.2
<i>Notropis heterodon</i>	Blackchin shiner	1	4.2
<i>Osmerus mordax</i>	Rainbow smelt	1	4.2
<i>Rhinichthys atratulus</i>	Blacknose dace	1	4.2
<i>Cottus cognatus</i>	Slimy sculpin	1	4.2
<i>Semotilus corporalis</i>	Fallfish	1	4.2
<i>Prosopium cylindraceum</i>	Round whitefish	1	4.2

Fig. 10. Frequency of occurrence of fish species in the Muskoka-Haliburton lakes compared with that of the lakes of the Bruce Peninsula. Species identity: 1. blacknose dace, fallfish, lake chub, round whitefish, slimy sculpin, trout-perch; 2. rainbow smelt; 3. lake herring, lake whitefish; 4. mottled sculpin; 5. brassy minnow; 6. rainbow trout; 7. burbot; 8. brook trout; 9. pearl dace; 10. lake trout; 11. northern redbelly dace; 12. smallmouth bass; 13. creek chub; 14. brown bullhead; 15. golden shiner; 16. white sucker; 17. pumpkinseed; 18. yellow perch; 19. alewife, black crappie, emerald shiner, rainbow smelt, redbfin shiner, river chub, sand shiner; 20. logperch; 21. carp; 22. bowfin, mimic shiner, yellow bullhead; 23. least darter; 24. walleye; 25. finescale dace; 26. banded killifish, johnny darter; 27. tadpole madtom; 28. fathead minnow; 29. blackchin shiner; 30. largemouth bass; 31. brook stickleback; 32. common shiner; 33. blacknose shiner; 34. northern pike; 35. bluntnose minnow; 36. central mudminnow; 37. rock bass; 38. Iowa darter.

FIGURE NO. 10
See previous page for interpretation
of numbers

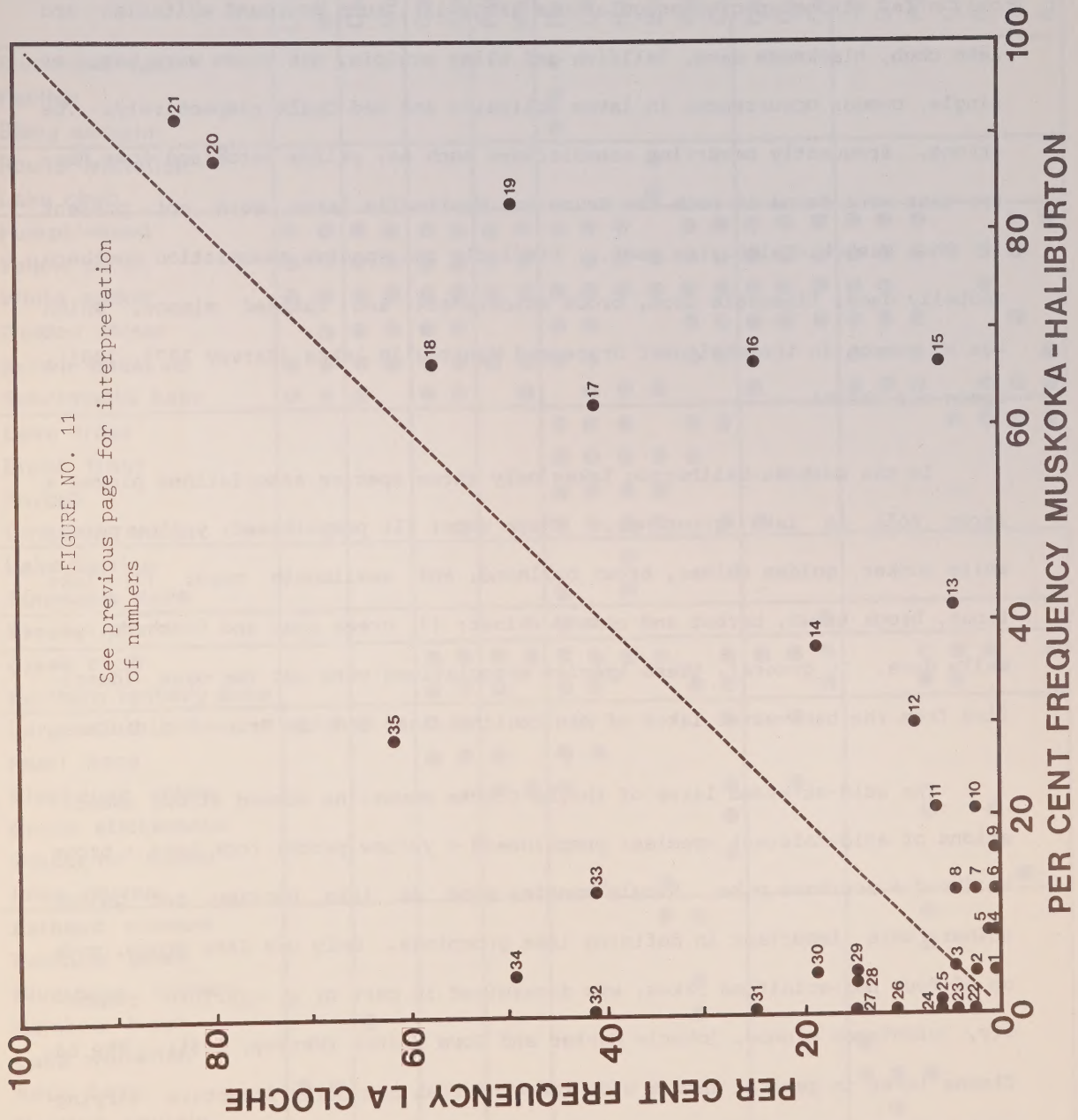


of occurrence). Some of the common species such as small-mouth bass (# 12) and yellow perch (# 18) were close to the line of equal frequency, but most species were quite dissimilar in frequency of occurrence in the two areas.

The comparison of fish frequency of occurrence between Muskoka-Haliburton and the acid-stressed La Cloche lakes was made also (Fig. 11). This showed the greater frequency of occurrence of fishes in Muskoka-Haliburton. The species closest to the line of equal frequency were the relatively acid-tolerant brown bullhead, pumpkinseed, and yellow perch. Among the cyprinids, a large family of relatively acid-sensitive fishes, the more acid tolerant creek chub, golden shiner, northern redbelly dace and common shiner were much better represented in the Muskoka-Haliburton lakes.

In analyses of this type it is difficult to separate the effects of zoogeography (i.e. opportunity of a species to invade a lake), mutual exclusion between species, physical environmental factors, and anthropogenic effects (including stocking and various stresses). It is clear enough that acid stress is the dominant variable involved in the reduced fish populations of the La Cloche lakes. That could not be said of the lake set examined from Muskoka-Haliburton. In terms of frequency of fish species occurrence, these lakes are closer to the hard-water lakes of the Bruce Peninsula.

Fig. 11. Frequency of occurrence of fish species in the Muskoka-Haliburton lakes compared with that of the acid-stressed La Cloche lakes. Species identity: 1. blackchin shiner, blacknose dace, fallfish, mottled sculpin, rainbow smelt, round whitefish, slimy sculpin; 2. trout-perch; 3. lake chub; 4. finescale dace; 5. brassy minnow; 6. fathead minnow; 7. rainbow trout; 8. brook stickleback; 9. burbot; 10. brook trout; 11. blacknose shiner; 12. common shiner; 13. northern redbelly dace; 14. lake trout; 15. creek chub; 16. golden shiner; 17. smallmouth bass; 18. brown bullhead; 19. white sucker; 20. pumpkinseed; 21. yellow perch; 22. mimic shiner; 23. rainbow darter; 24. central mudminnow; 25. logperch; 26. walleye; 27. bluegill; 28. largemouth bass; 29. lake whitefish; 30. bluntnose minnow; 31. johnny darter; 32. northern pike; 33. Iowa darter; 34. lake herring; 35. rock bass.



Fish Communities

Fish species associations were defined by cluster analysis using Jaccard's coefficient of similarity. The Muskoka-Haliburton data set yielded only a few strong species associations (Fig. 12), such as round whitefish and lake chub, blacknose dace, fallfish and slimy sculpin, but these were based on single, common occurrences in lakes Solitaire and Red Chalk respectively. The strong, frequently occurring associations such as: yellow perch and Iowa darter that were found in both the Bruce and Manitoulin lakes, were not present in the Muskoka-Haliburton set. Similarly the species association northern redbelly dace, finescale dace, brook stickleback, and fathead minnow, which was so common in the shallower Bruce and Manitoulin lakes (Harvey 1978, 1981), again was absent.

In the Muskoka-Haliburton lakes only three species associations played a large role in lake groupings. These were: (1) pumpkinseed, yellow perch, white sucker, golden shiner, brown bullhead, and smallmouth bass; (2) lake trout, brook trout, burbot and common shiner; (3) creek chub and northern redbelly dace. In general, these species associations were not the ones identified from the hard-water lakes of Manitoulin Island and the Bruce Peninsula.

The acid-stressed lakes of the La Cloche Mountains showed strong associations of acid-tolerant species: pumpkinseed + yellow perch; rock bass + brown bullhead + northern pike. Single species such as lake herring and golden shiner were important in defining lake groupings. Only one lake group, made up of four non-acidified lakes, was determined in part by a cyprinid community, bluntnose minnow, johnnie darter and Iowa darter (Harvey, 1981). The La Cloche lakes in general show a wide range of fish community structure varying from several (five or six) associations in the least acidified, to one or zero

	Leech	McKay	Chub	Moot	Dickie	Fawn	Poker	Heaney	Red Chalk	Little Clear	Harp	Solitaire	Bigwind	Crosson	Healey	Gullfeather	Cinder	Leonard	Glen	Plastic	Clear	Buck	Walker	Basshaunt
Blacknose dace									•															
Fallfish									•															
Slimy sculpin									•															
Round whitefish												•												
Lake chub												•												
Pumpkinseed	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Yellow perch	•	•	•	•	•	•	•	•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
White sucker	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Golden shiner		•	•	•	•	•			•	•			•	•	•	•	•	•	•	•			•	•
Brown bullhead	•	•	•	•	•	•	•	•	•	•			•	•	•	•		•	•	•				•
Smallmouth bass	•	•	•		•	•		•		•	•	•			•	•	•	•	•	•		•	•	•
Lake trout									•	•	•		•	•							•	•	•	•
Brook trout									•	•	•	•	•											
Burbot									•	•	•	•	•											
Common shiner						•			•	•	•	•		•	•									
Lake herring											•													
Finescale dace									•		•													
Brassy minnow									•								•							
Creek chub					•	•	•	•	•	•	•	•		•	•	•	•			•	•	•	•	•
Northern redbelly dace					•	•	•		•	•			•	•			•			•	•			
Largemouth bass	•	•	•	•	•	•								•		•								
Pearl dace					•	•	•		•	•														
Blacknose shiner							•	•	•					•		•								
Brook stickleback														•					•			•		
Blackchin shiner														•										
Iowa darter										•		•											•	
Fathead minnow											•	•								•				
Rainbow smelt																				•				
Bluntnose minnow													•											
Rainbow trout			•										•						•					
Lake whitefish																		•	•					
Rock bass	•	•																•	•	•				
Mottled sculpin																			•					
Trout perch					•																			

Fig. 12. Matrix of lakes and fish species, based on cluster analysis using Jaccard's coefficient of similarity, Muskoka-Haliburton twenty-four lake set.

species associations in the more acid-stressed.

The Muskoka-Haliburton lakes did not correspond closely to either of the hard-water or acid-stressed patterns of fish communities described above. Only three species associations were important in defining lake groupings, about half as many as in the hard-water lakes, and with only four cyprinids involved. In this sense the Muskoka-Haliburton lakes resemble more closely the lakes of the La Cloche.

Age-Class Composition

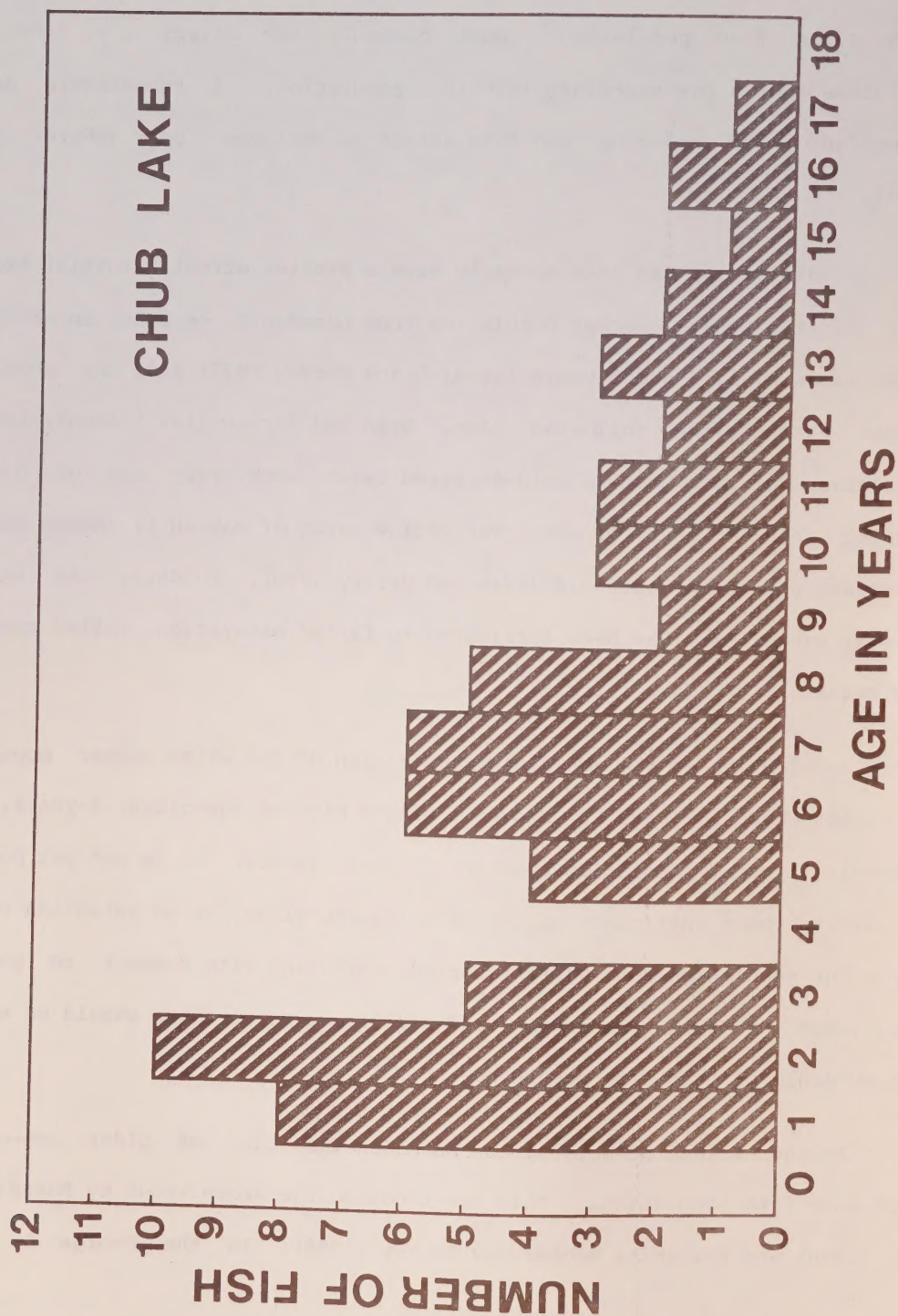
A variety of environmental factors can influence the age-class composition of a fish population. Most commonly the effect is to prevent the recruitment of a new age-class into the population. A temperature decline coincident with spawning had this effect on smallmouth bass (Shuter et al., 1980).

Acidification has been shown to have a similar effect. Initial examination of the white sucker population from Lumsden L. revealed an absence of age-classes 0, 1, 2 and 5 years (Beamish and Harvey 1972) and the population became extinct the following year. Ryan and Harvey (1977) identified five populations of rock bass in acid-stressed lakes with very few or no fish younger than 5 years of age. The yellow perch of Patten L. showed only one age-class under six years old (Ryan and Harvey 1980). To date, the loss of younger age-classes has been attributed to failed maturation, failed spawning, and mortality of eggs or fry.

Examination of the age-class composition of the white sucker population of acid Chub L. (Fig. 13) showed a single missing age-class, 4-years, in an otherwise typical population spanning 17 year-classes. It is not yet possible to define the significance of this missing age-class, or to establish causality. The population does warrant period monitoring with respect to possible recurrence of this phenomenon, and additional populations should be sampled for evidence of this same occurrence.

Another effect of acid-stress has been the loss of older age-classes from some fish populations. This was reported for brown trout by Rosseland et al. (1980) and for white suckers by Harvey (1980). In the George L. white

Fig. 13. Age-class composition of the white sucker population in Chub Lake.



sucker population, the age-class composition declined from 14 years to 6, 1967-1979, and with 95% of the population in age-classes 2 and 3 years. In the Muskoka-Haliburton lakes, acid Crosson L. showed a truncated age-class composition (Fig. 14) with almost all fishes in age-classes 1-5 years, and the majority of fishes 2-3 years old. In contrast, the less acid lakes Harp and Red Chalk showed 10 and 13 age-classes respectively. The unusual age-class composition of Crosson L. warrants the extension of the age analysis to additional populations, especially those in the pH range 5.0-5.5.

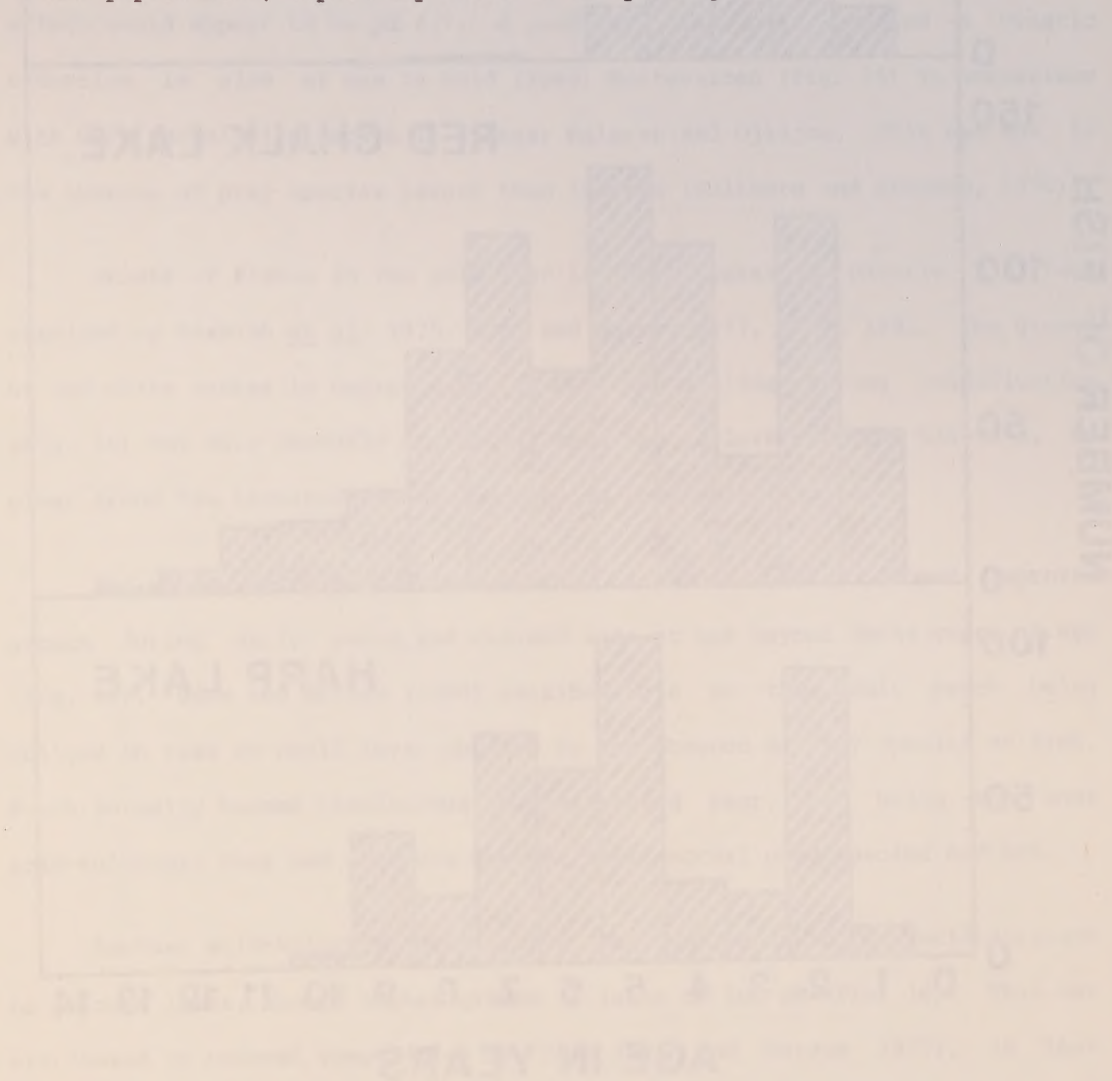
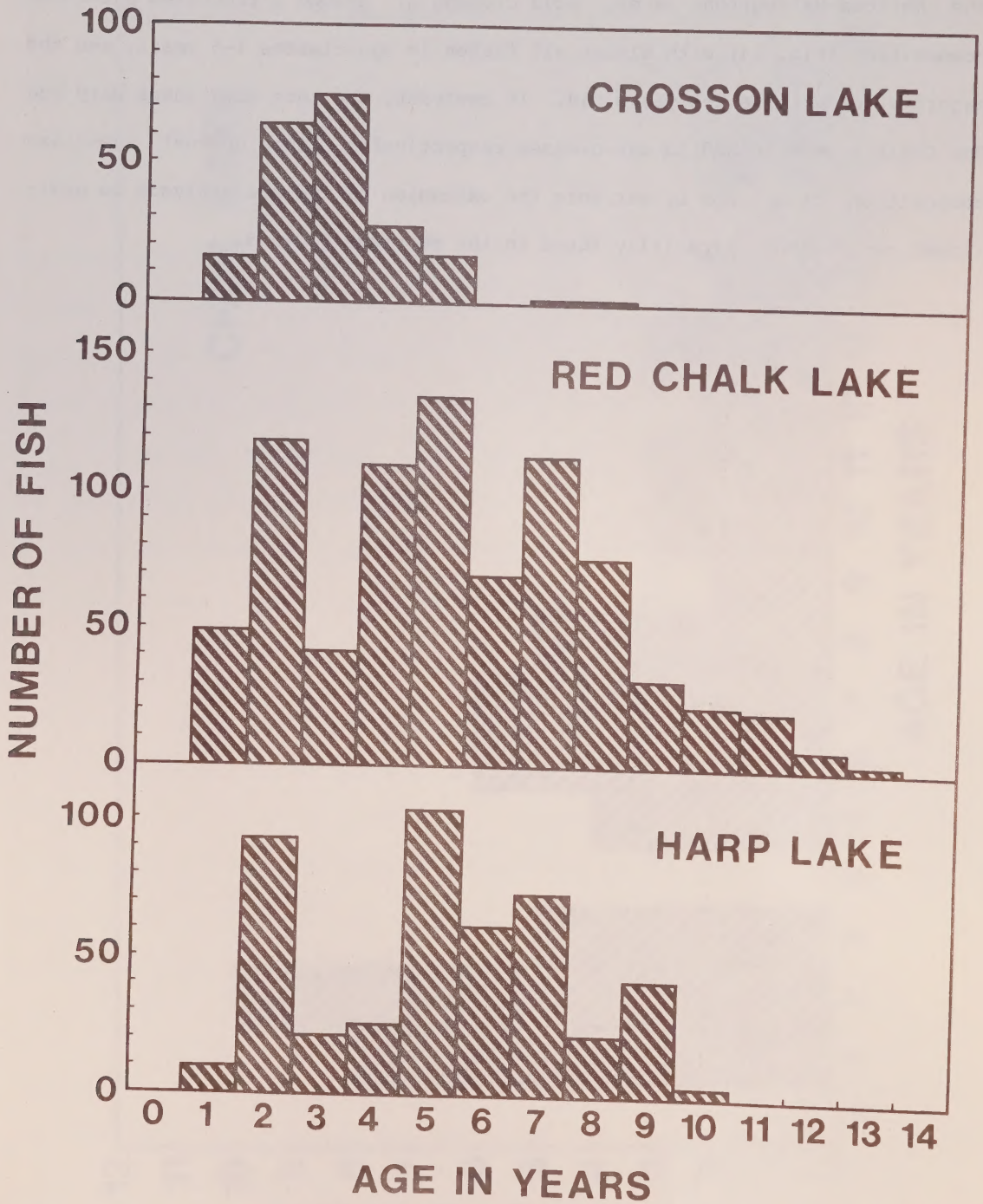


Fig. 14. Age-class composition of the white sucker populations in lakes Crosson, Red Chalk and Harp.



Growth of Fishes

It has been known for some years that the growth of fishes is affected by lake acidification. The work of Almer (1972) identified the departure of perch growth from normal in Swedish lakes (Fig. 15). The increased growth of this species in acid lakes was attributed to reduced competition for food. The small population of older perch in (lake) Stora Skarsjon however did not show this effect. For the acid-tolerant perch, the threshold for the growth effect would appear to be pH 4.7. A predator, the pike, showed a drastic reduction in size at age in acid (lake) Morteavatten (Fig. 15) in comparison with more normal pike growth in (lakes) Malaren and Ojesjon. This was due to the absence of prey species larger than insects (Hultberg and Stenson, 1970).

Growth of fishes in the acidified La Cloche lakes of Ontario has been examined by Beamish et al. 1975, Ryan and Harvey 1977, 1980, 1981. The growth of the white sucker in George Lake tended to decline during acidification (Fig. 16) but more recently growth has returned to levels of the mid-60's. No clear trend has resulted despite changes in population size.

The yellow perch populations of the La Cloche lakes showed improved growth during early years and reduced size at age beyond three years of age (Fig. 16). Ryan and Harvey (1980) ascribed this to the adult perch being obliged to feed on small invertebrates in the absence of prey species of fish. Perch normally become piscivorous in their third year, but being the most acid-tolerant, they had survived whereas their normal prey species had not.

Another acid-tolerant species, the rock bass, also in the acid-stressed La Cloche lakes, showed better growth in lakes of low pH (Fig. 16). This was attributed to reduced competition for food (Ryan and Harvey 1977), in that

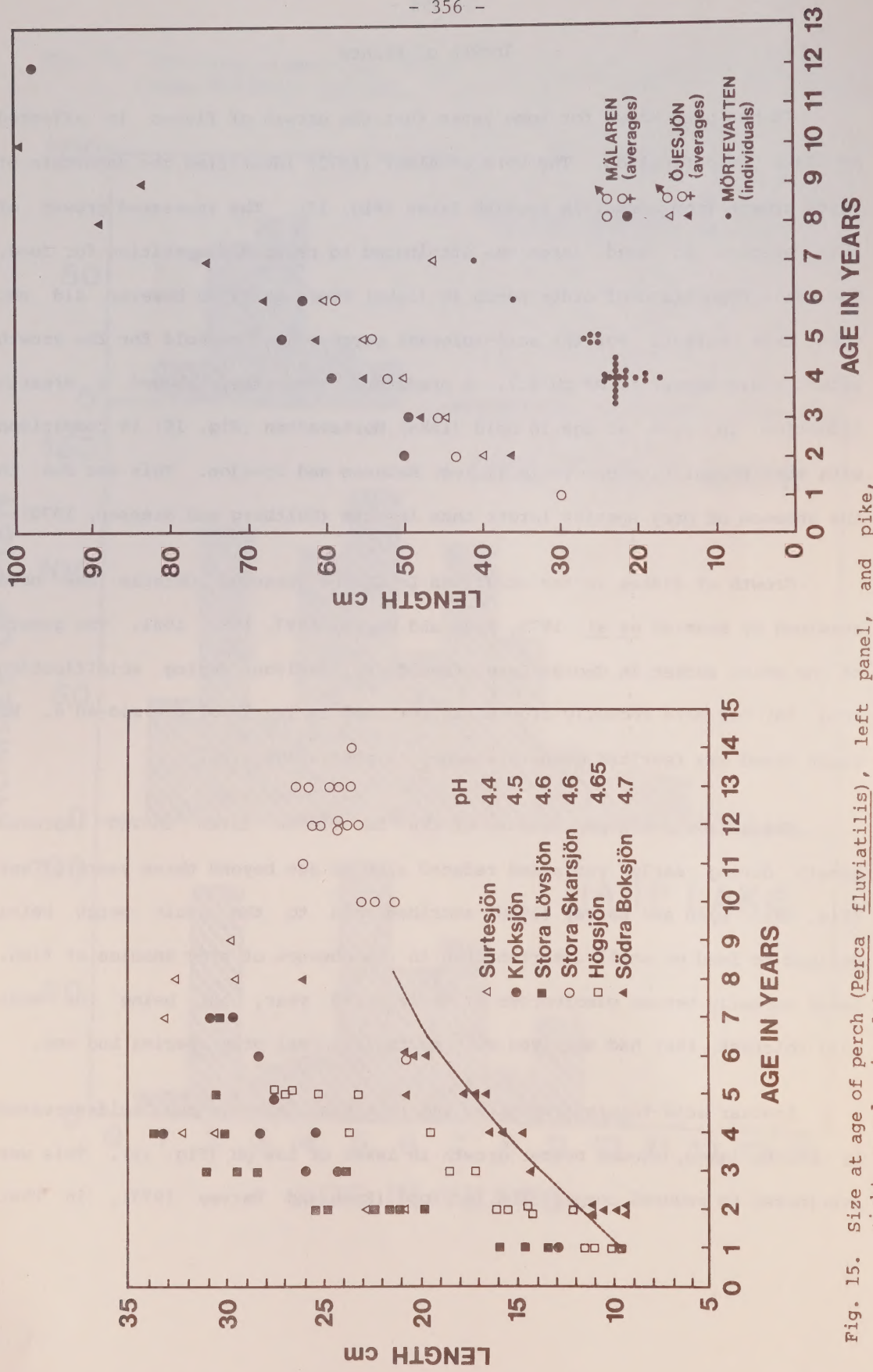


Fig. 15. Size at age of perch (*Perca fluviatilis*), left panel, and pike, right panel, in lakes over a range of pH. Sources: Almer, 1972; Hultberg and Stenson, 1970; Svardson, 1964.

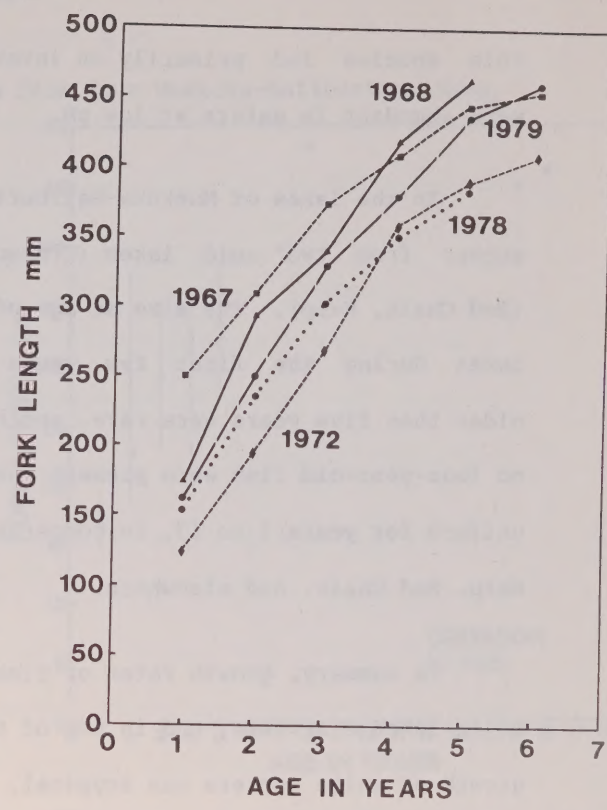
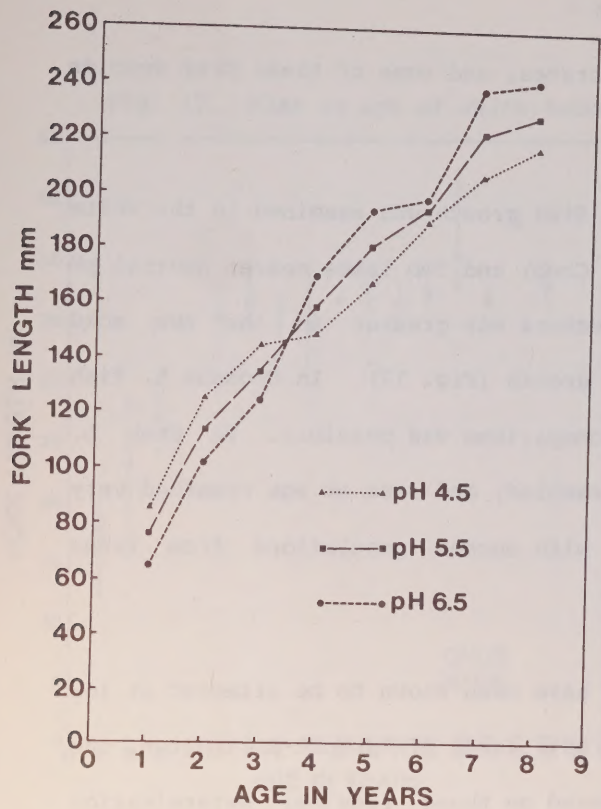
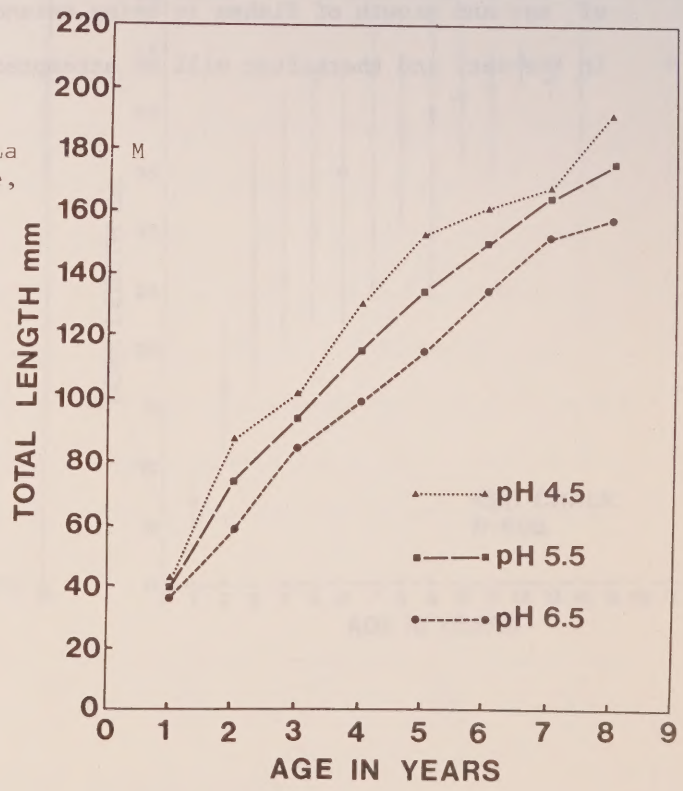


FIGURE NO. 16

Size at age of yellow perch (upper left) and rock bass (lower right) populations in relation to pH for La Cloche Mountain lakes. Size at age, white sucker (upper right) George Lake. Sources: Ryan and Harvey, 1977; Ryan and Harvey, 1980; Beamish et al., 1975; Harvey and Lee, 1980.

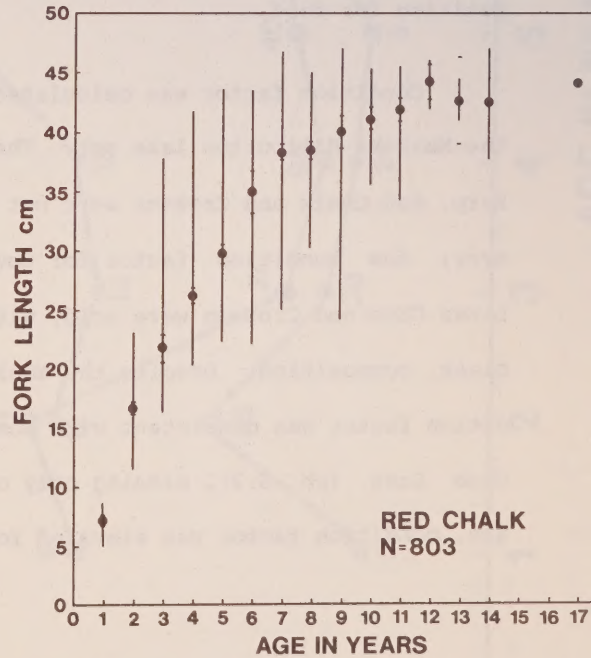
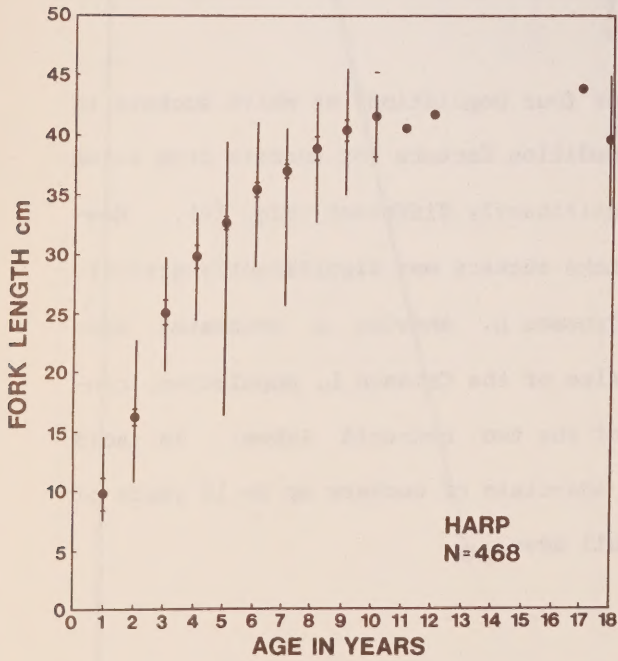
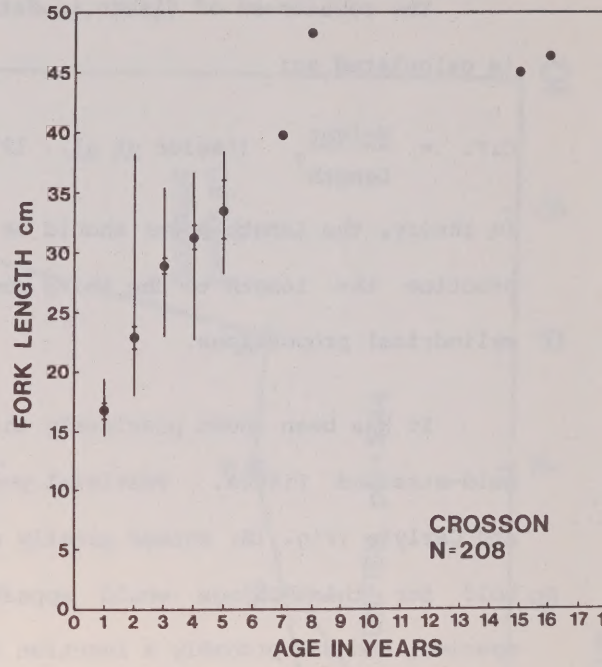
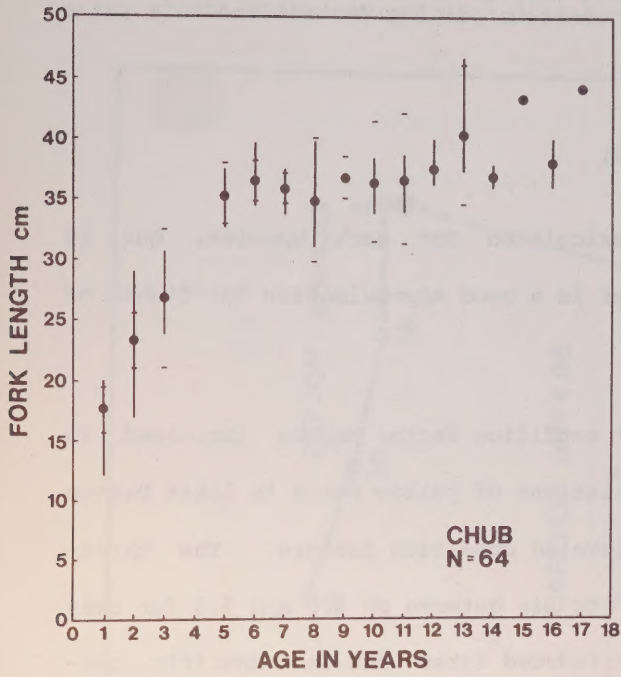


this species fed primarily on invertebrates, and some of these prey species were abundant in waters at low pH.

In the lakes of Muskoka-Haliburton fish growth was examined in the white sucker from two acid lakes (Crosson, Chub) and two lakes nearer neutral pH (Red Chalk, Harp). The size at age of suckers was greater in the two acid lakes during the first few years of growth (Fig. 17). In Crosson L. fish older than five years were rare, and no comparison was possible. In Chub L. no four-year-old fish were present when sampled, and size at age remained very uniform for years 5 to 17, in comparison with sucker populations from lakes Harp, Red Chalk, and elsewhere.

In summary, growth rates of fishes have been shown to be affected at low pH in lakes elsewhere, and in two of the acid lakes of Muskoka-Haliburton, the growth of white suckers was atypical. Based on these results, determination of age and growth of fishes is being extended to white suckers in other lakes in the set, and thereafter will be attempted for additional species.

Fig. 17. Size at age of white suckers from four Muskoka-Haliburton lakes.



Fish Condition and Lake pH

The robustness of fishes is defined as 'condition factor' and this ratio is calculated as:

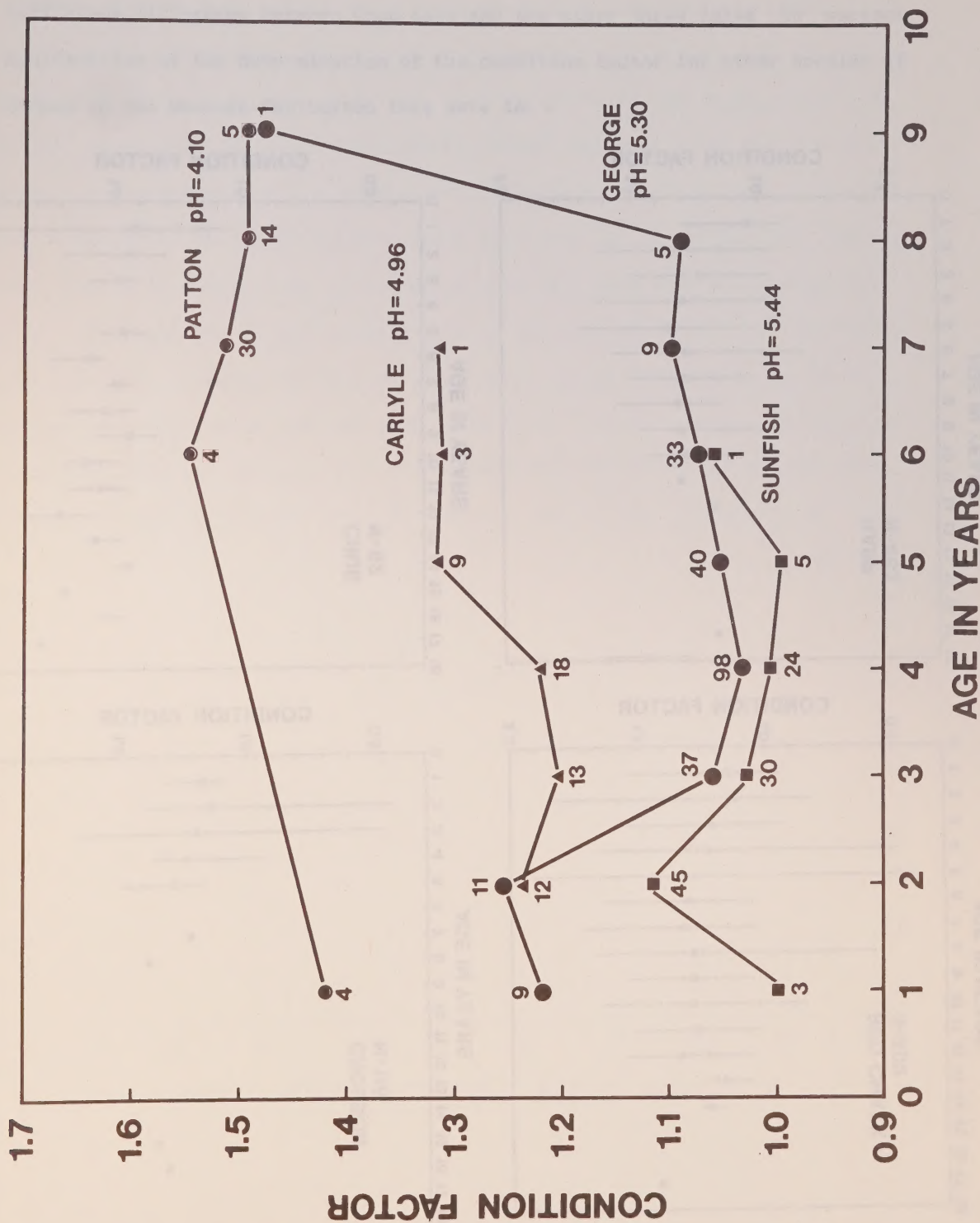
$$\text{C.F.} = \frac{\text{Weight}}{\text{Length}^3} \quad (\text{Lagler et al., 1972})$$

In theory, the length power should be calculated for each species, but in practice the length to the third power is a good approximation for fishes of cylindrical proportions.

It has been shown previously that condition factor may be increased in acid-stressed fishes. Vestigial populations of yellow perch in lakes Patton and Carlyle (Fig. 18) showed greatly elevated condition factors. The threshold for this change would appear to lie between pH 5.0 and 5.3 for this species, and was probably a function of reduced inter- and intraspecific competition for food.

Condition factor was calculated for four populations of white suckers in the Muskoka-Haliburton lake set. The condition factors for suckers from lakes Harp, Red Chalk and Crosson were not significantly different (Fig. 19). However, the condition factor for Chub Lake suckers was significantly greater. Lakes Chub and Crosson were acid, with Crosson L. showing a truncated age-class composition. Despite the small size of the Crosson L. population, condition factor was consistent with that of the two non-acid lakes. In acid Chub Lake (pH 5.3), missing only one age-class of suckers up to 18 years of age, condition factor was elevated for all ages.

Fig. 18. Condition factor of yellow perch in relation to lake pH, four lakes, La Cloche Mountains. Source: Harvey, 1981.



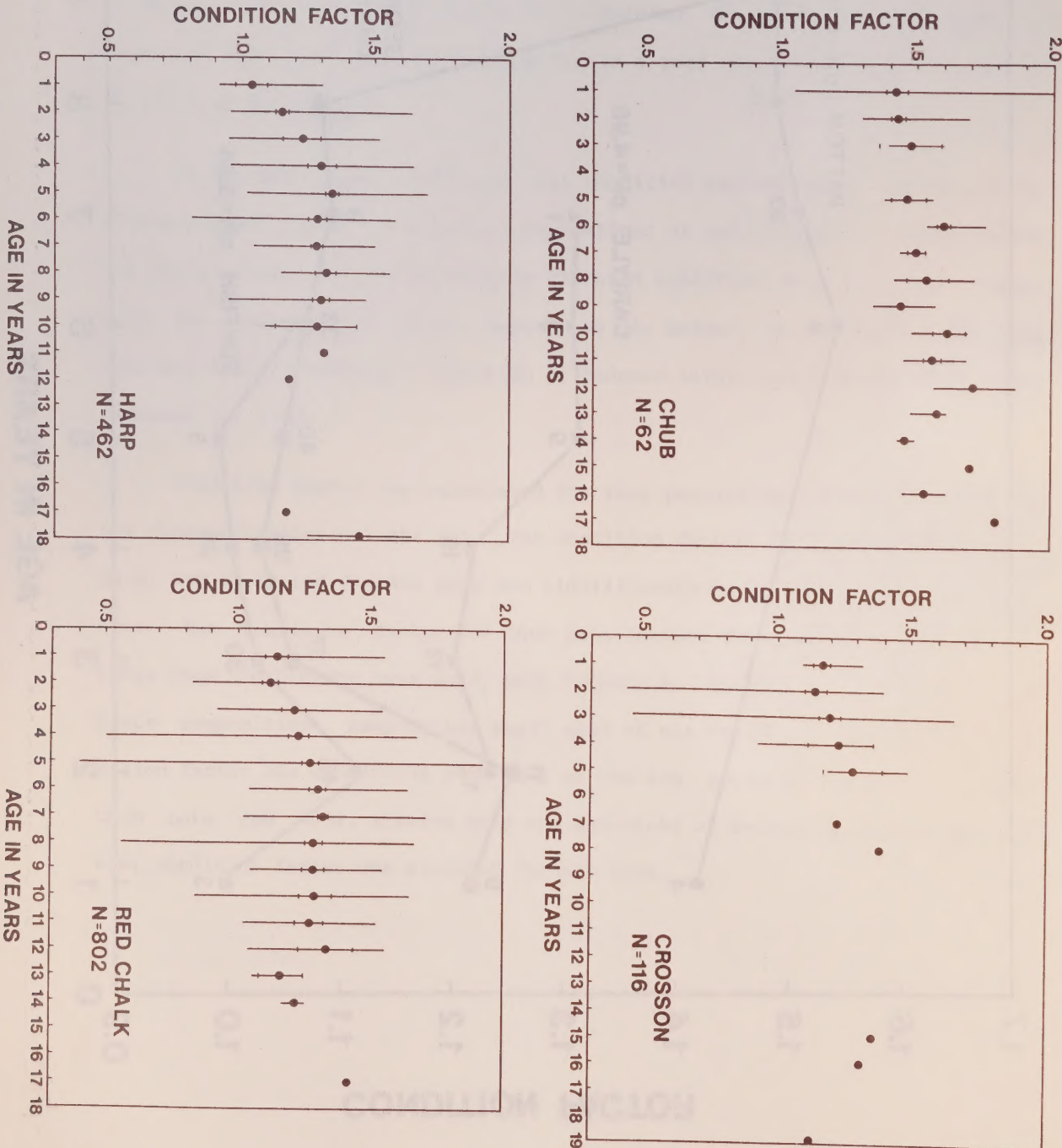
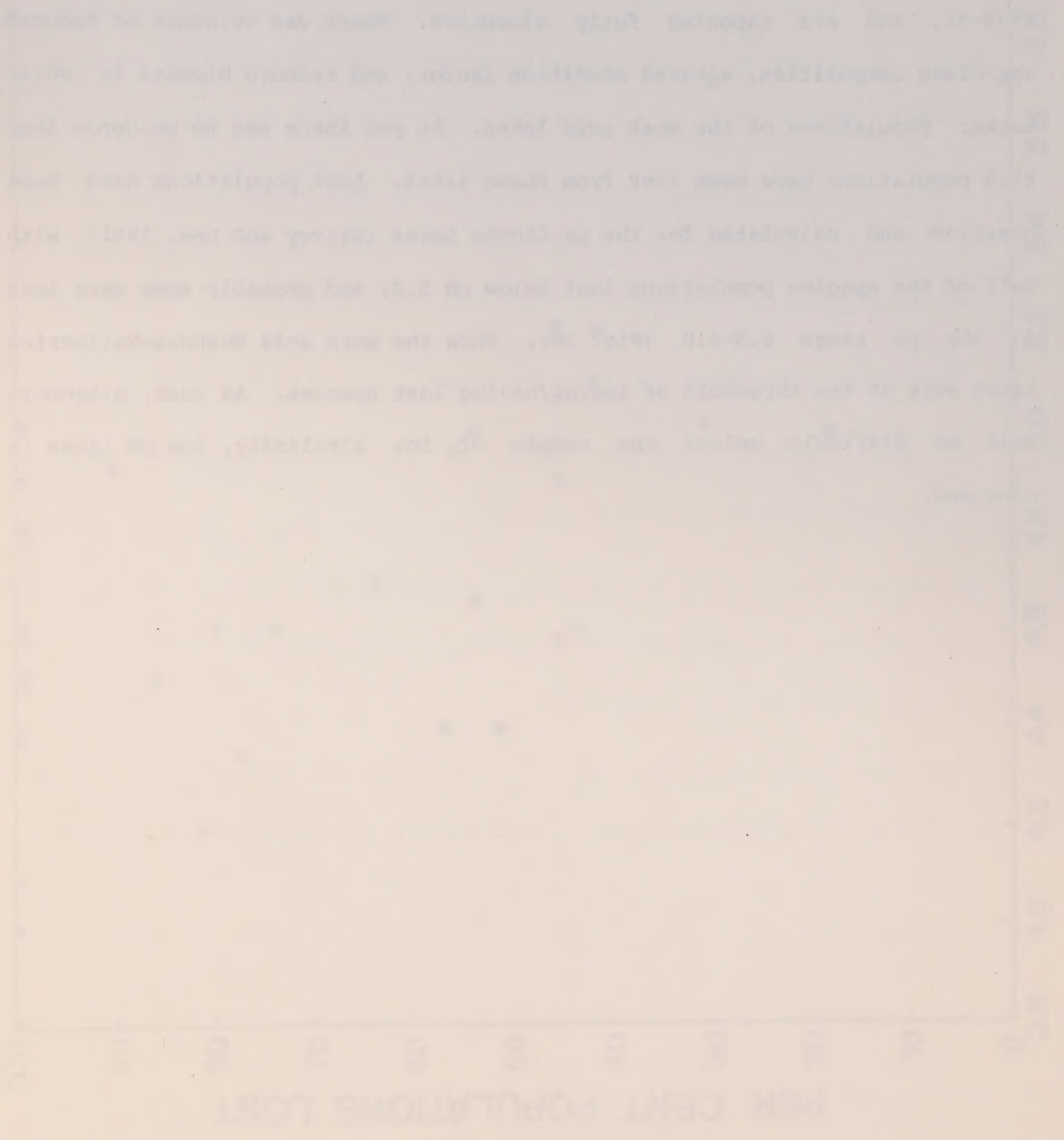


Fig. 19. Condition factor of white suckers, four lakes, Muskoka-Haliburton.

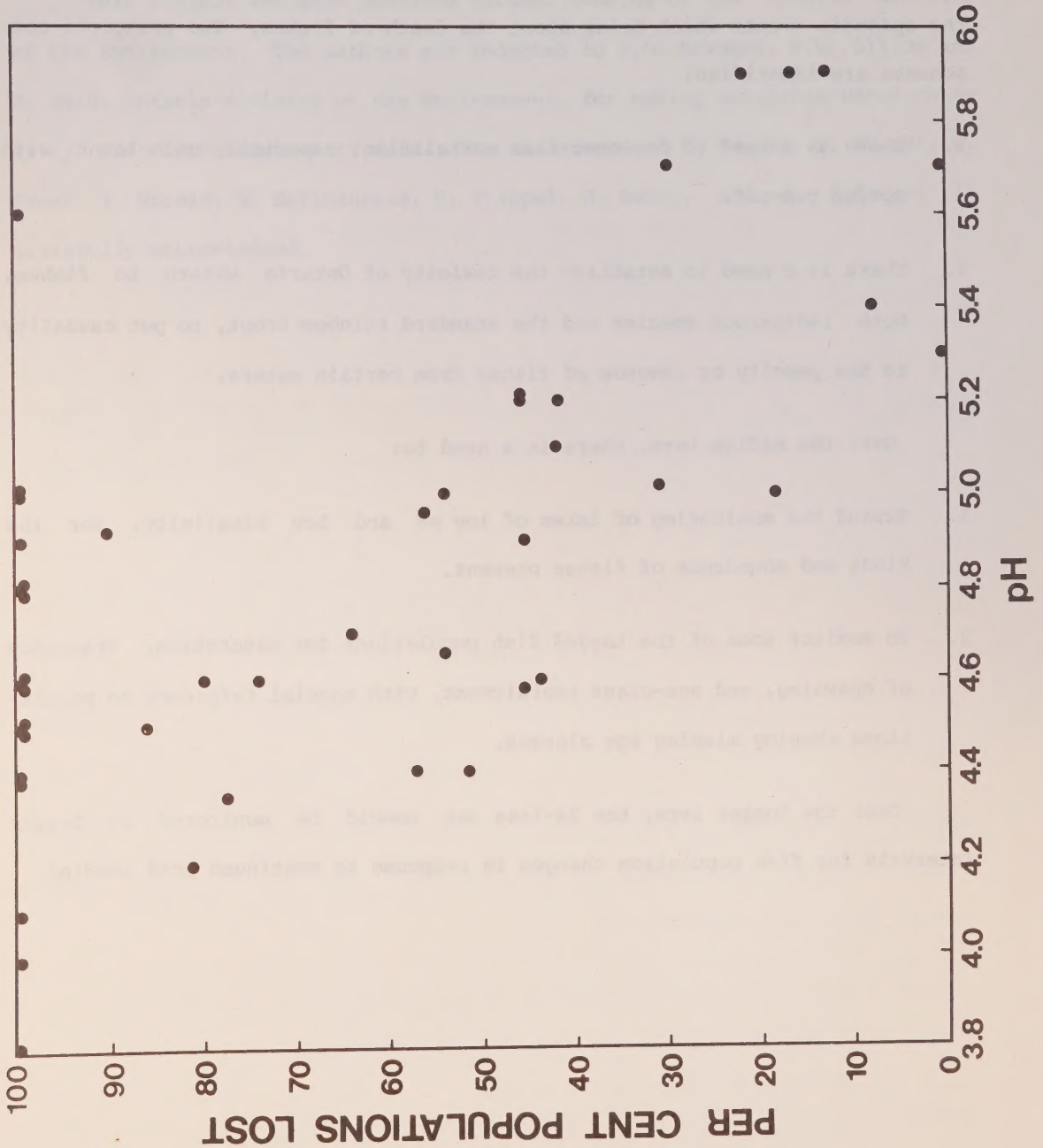
These results are not consistent with a simple explanation of lake pH determining the condition factor of fish via competition for food. There is sufficient difference between Chub Lake and the other three lakes to warrant continuation of the determination of the condition factor for other species of fishes in the Muskoka-Haliburton lake set.



Summary

There was evidence of acid precipitation induced stress on the fishes of some of the 24 study lakes, Muskoka-Haliburton. The most serious was the aluminum-induced fish kills of Plastic Lake, which have been recorded annually 1978-81, and are reported fully elsewhere. There was evidence of reduced age-class composition, altered condition factor, and reduced biomass in white sucker populations of the most acid lakes. As yet there was no evidence that fish populations have been lost from these lakes. Lost populations have been observed and calculated for the La Cloche Lakes (Harvey and Lee, 1981), with half of the species populations lost below pH 5.0, and probably some were lost in the pH range 5.5-6.0 (Fig. 20). Thus the more acid Muskoka-Haliburton lakes were at the threshold of losing/having lost species. As such, diagnosis will be difficult unless the sample of low alkalinity, low pH lakes is expanded.

Fig. 20. Calculated lost populations of fishes from the La Cloche Mountain lakes. Source: Harvey and Lee, 1981.



Recommendations

Over the short term, future monitoring should be directed at quantifying the episodic events which bring about the death of fishes. Two principle components are identified:

1. There is a need to document fish mortalities, especially coincident with spring run-off.
2. There is a need to establish the toxicity of Ontario waters to fishes, both indigenous species and the standard rainbow trout, to put causality to the paucity or absence of fishes from certain waters.

Over the medium term, there is a need to:

1. Expand the monitoring of lakes of low pH and low alkalinity, for the kinds and abundance of fishes present.
2. To monitor some of the tagged fish populations for maturation, frequency of spawning, and age-class recruitment, with special reference to populations showing missing age classes.

Over the longer term, the 24-lake set should be monitored at 5-year intervals for fish population changes in response to continued acid loading.

Acknowledgements

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USE OF FRESHWATER CLAMS IN MONITORING TRACE CONTAMINANT
SOURCE AREAS

by

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SUMMARY

Freshwater clams (Elliptio complanatus) from Balsam Lake were placed in cages and anchored at a number of sites in the Niagara River during 1980. Clams were exposed to river water for 1 to 101 days before their removal and analysis for trace organic and inorganic contaminants concentrations in soft tissues.

Clams accumulated significant levels of PCBs after only two days' exposure to river water. However, the highest concentrations of PCBs, hexachlorobenzene, α -BHC, dieldrin, α and γ -chlordane, endrin and heptachlor epoxide were generally found in clams after 16 days' exposure to water.

Regional differences in concentrations were only evident for a few inorganics (arsenic, copper and zinc) and only after much longer exposure periods (i.e. $\sim$ 100 days) than were necessary for PCBs and organochlorine pesticides.

Caged clams have proven to be a useful addition to other biomonitoring organisms used in the Niagara River (i.e. young-of-the-year spottail shiners (Notropis hudsonius) and the filamentous alga Cladophora) to detect source areas of trace contaminants which eventually enter the Lake Ontario ecosystem.

Some of the practical considerations in the use of freshwater clams as biomonitors are discussed.

INTRODUCTION

Marine and estuarine species of clams and oysters have been used in numerous studies as indicators of coastal pollution because of their ability to bioconcentrate such contaminants as heavy metals, pesticides, PCBs, PAHs and petrochemicals (Blumer et al., 1970; Butler, 1973; Marchand et al., 1976; Bayne, 1978, Goldberg et al., 1978). This results in part from their filter-feeding habit, which exposes tissues to both aqueous- and particulate-borne contaminants.

Although not as intensively utilized as their marine counterparts, freshwater clams and mussels have been receiving increasing attention as biomonitoring organisms (Bedford et al., 1968; Curry, 1977/78; Foster and Bates, 1978; Forester, 1980; Heit et al., 1980; Leard et al., 1980).

This paper illustrates the use of one freshwater clam species (Elliptio complanatus) in monitoring trace contaminant source areas during a 1980 study of the Niagara River. All field work was carried out by Integrated Exploration personnel under contract to the Ministry of the Environment's Water Resources Branch. This study was part of a larger biomonitoring investigation undertaken by the Ministry of the Environment, Water Resources Branch using, in addition to clams young-of-the-year spottail shiner fish (Notropis hudsonius) and filamentous attached algae (Cladophora) (Canada-Ontario Review Board, 1981).

METHODS

Collection of Clams

Freshwater clams of the species Elliptio complanatus (Pelecypoda: Unionidae) in the size range 6.5 to 7.2 cm in length were collected from the shallows (~2 m depth) of Balsam Lake in southern Ontario (Victoria County) during August 1980. Collection was carried out by divers using SCUBA or a hookah diving system (air supplied from surface air compressor via an air hose).

As a control, 20 of the Balsam Lake clams were individually weighed, measured and then shucked for later analysis.

Clams were kept constantly submerged in Balsam Lake water while they were being collected, sorted and stored for transportation to the study area sites along the Niagara River.

The clams were transported in Balsam Lake water to the Niagara River within 24 hours of their collection.

Deployment and Recovery of Clams

A number of sites in both the upper and lower sections of the Niagara River were selected so that clams would be situated downstream of potential trace contaminants source areas (e.g. upper Niagara River: Tonawanda Channel, Buffalo River mouth). Clams located at the Welland River site were actually exposed to Niagara River water, since flow is reversed in this section of the river (see Figure 1). The background control site was located in Thunder Bay, Lake Erie on the basis of previous analytical results obtained for another biomonitoring organism, young-of-the-year spottail shiners (see Sun et al, 1981). Figure 1 shows the location of the clam biomonitoring sites.

Stations for the clam exposures were located relatively close to shore, in approximately 2 m of water, similar to the depth at which clams were collected in Balsam Lake.

A maximum of 10 clams were placed in each galvanized wire cage (22x21x15 cm).

At each station, a number of cages were secured to a nylon rope by plastic fasteners looped through the braiding of the rope and the bars of the cage. An orange float attached to the end of the rope served as a submerged marker for later recovery. A diver then anchored this array to the bottom by tethering to a stainless steel auger. Augers were found to be stronger, lighter and more readily deployed than driving in stakes or using blocks as weights and could be used in a variety of bottom types including coarse gravel, sand, clay, mud and rocks.

Clams were exposed to water for varying time periods, including 1, 2, 4, 8, 16, 32, 64 and 101 days (August 13 to November 21, 1980) before their removal and analysis for trace organic and inorganic contaminants concentrations in their soft tissues. At the end of each exposure period, two cages of 10 clams each were removed and the clams weighed, measured and placed in plastic bags placed over ice water. Shucking of clams was carried out at the Guelph

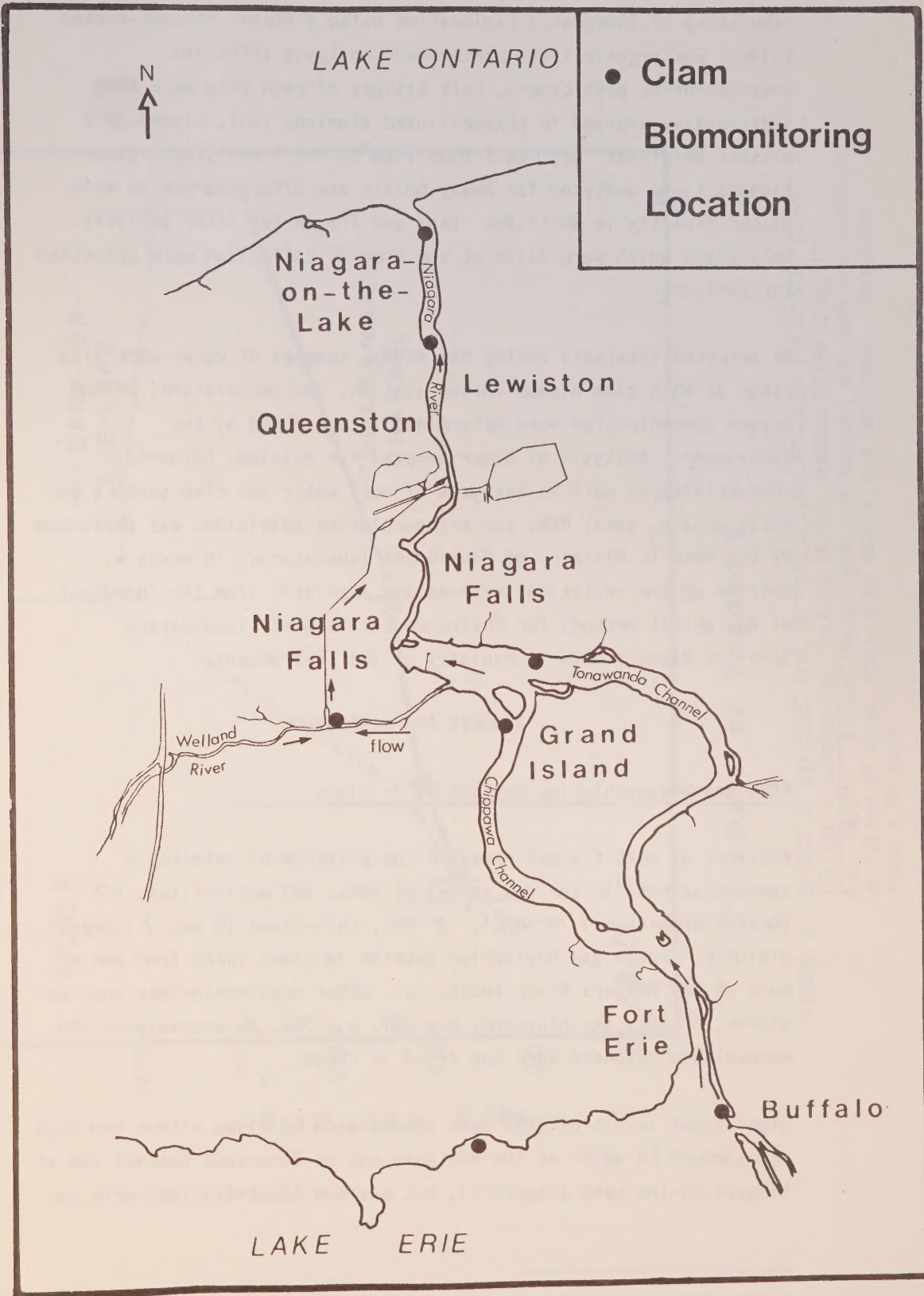


FIGURE 1. NIAGARA RIVER FRESHWATER CLAM BIOMONITORING LOCATIONS - 1980.

laboratory of Integrated Exploration using a clean, solvent-rinsed knife. For organic trace contaminant analysis (PCBs and organochlorine pesticides), soft tissues of each clam were then individually-wrapped in hexane-rinsed aluminum foil, placed in a plastic Whirl-Pak bag and frozen (-20°C) until analyzed. Clam tissues to be analyzed for heavy metals and other inorganics were placed directly in Whirl-Pak bags and frozen for later analysis. Only clams which were alive at the time of collection were processed for analysis.

At selected intervals during the study, samples of water were also taken at each clam biomonitoring station, and temperature, pH and oxygen concentration were determined in the field by the contractor. Analysis of water samples for calcium, hardness, conductivity, as well as analysis of both water and clam samples for heavy metals, total PCBs and organochlorine pesticides was performed by the Ontario Ministry of Environment laboratories in Rexdale. Details of the analytical methods are available from the "Handbook of Analytical Methods for Environmental Samples" (Laboratory Services Branch, Ontario Ministry of the Environment).

RESULTS AND DISCUSSION

PCBs and Organochlorine Pesticides in Clams

Analyses of soft tissues revealed the presence of detectable concentrations (in the ppb range) of PCBs, DDT metabolites, HCB (hexachlorobenzene), α -BHC*, γ -BHC, chlordanes (α and γ isomers), dieldrin, endrin and heptachlor epoxide in clams taken from one or more of the Niagara River locations. Other organochlorines such as aldrin, β -BHC, oxychlordane, o,p-DDT, p,p-DDT, β -endosulphan and endosulphan sulphate were not found in clams.

Significant levels of PCBs were accumulated by clams within two days of exposure to water at the northern end of Tonawanda Channel and at Niagara-on-the-Lake (Figure 2), but maximum concentrations were not

* BHC (HCH) = hexachlorocyclohexane

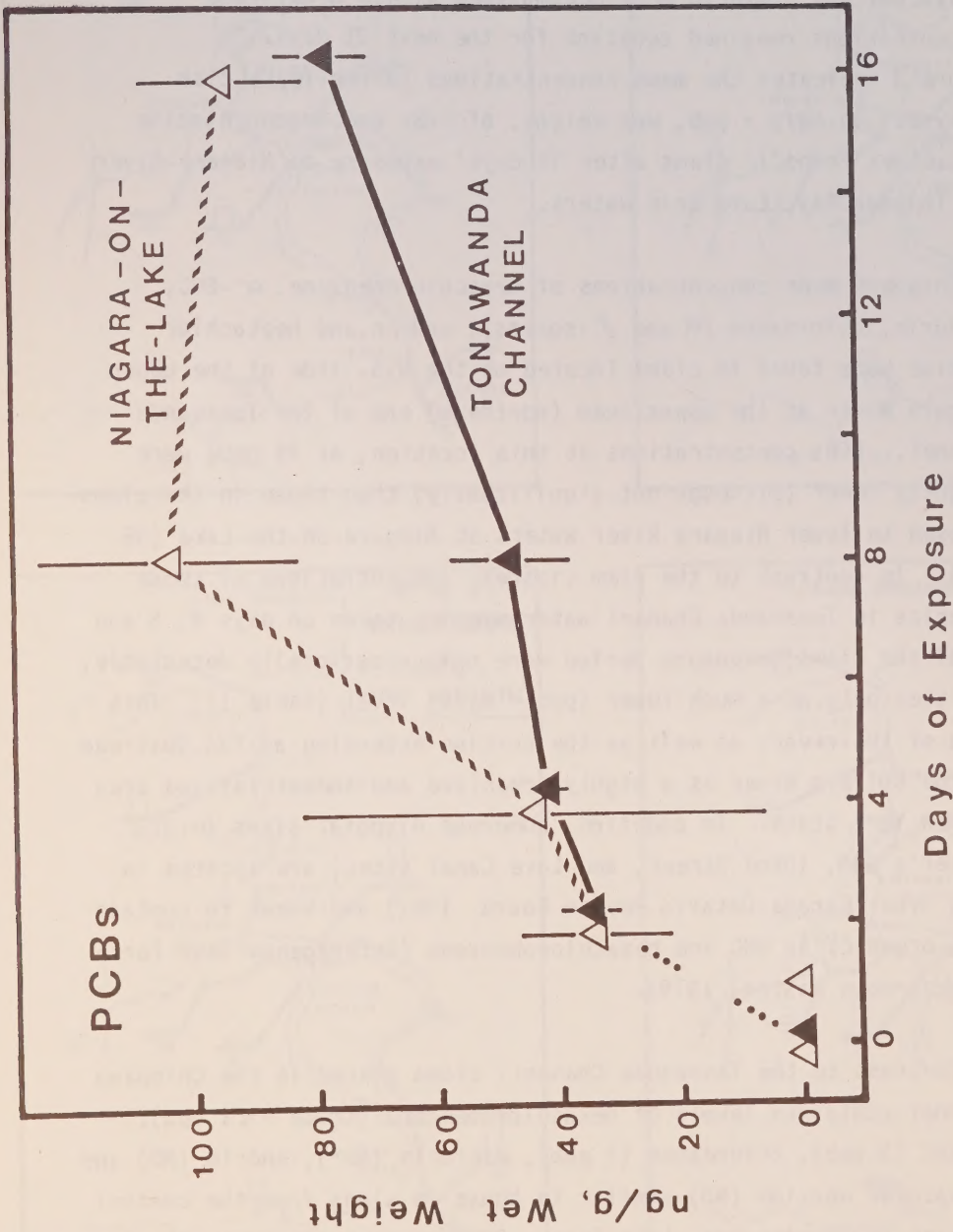


FIGURE 2. EFFECT OF EXPOSURE TIME ON PCBs ACCUMULATION BY FRESHWATER CLAMS (*Elliptio complanatus*) PLACED IN THE NIAGARA RIVER (Aug. 12 - Aug. 28/80). Values (ng/g = ppb, wet weight) are mean and standard deviation of three whole clam soft tissue analyses. Detection limit = 20 ng/g.

observed in tissues until 8 to 16 days' exposure had elapsed. This was also generally true of the organochlorine pesticides. Curry (1977/78) in a study involving E. complanatus at the mouths of the Humber and Moira Rivers, found that significant concentrations of PCBs, Σ DDT and dieldrin were accumulated within 8 days and concentrations remained constant for the next 21 days.

Figure 3 indicates the mean concentrations (3 replicate clam analyses) in ng/g = ppb, wet weight, of PCBs and organochlorine pesticides found in clams after 16 days' exposure to Niagara River and Thunder Bay, Lake Erie waters.

The highest mean concentrations of hexachlorobenzene, α -BHC, dieldrin, chlordanes (α and β isomers), endrin and heptachlor epoxide were found in clams located on the U.S. side of the upper Niagara River at the downstream (northern) end of the Tonawanda Channel. PCBs concentrations at this location, at 79 ppb, were slightly lower (although not significantly) than those in the clams exposed to lower Niagara River waters at Niagara-on-the-Lake (95 ppb). In contrast to the clam tissues, concentrations of these organics in Tonawanda Channel water samples taken on days 4, 8 and 16 of the clams' exposure period were only occasionally detectable, and then only at a much lower (ppt = ng/L) level (Table 1). This area of the river, as well as the portion extending as far upstream as the Buffalo River is a highly-urbanized and industrialized area of New York State. In addition, numerous disposal sites (e.g. Hooker's S&N, 102nd Street, and Love Canal sites) are located in this area (Canada-Ontario Review Board, 1981) and known to contain such organics as BHC and hexachlorobenzene (Interagency Task Force on Hazardous Wastes, 1979).

In contrast to the Tonawanda Channel, clams placed in the Chippawa Channel contained levels of hexachlorobenzene (trace = <1 ppb), α -BHC (5 ppb), chlordanes (2 ppb), dieldrin (ND*), endrin (ND) and heptachlor epoxide (ND) similar to those in clams from the control station in Thunder Bay, Lake Erie. PCBs concentrations in clams

* ND = Not detected

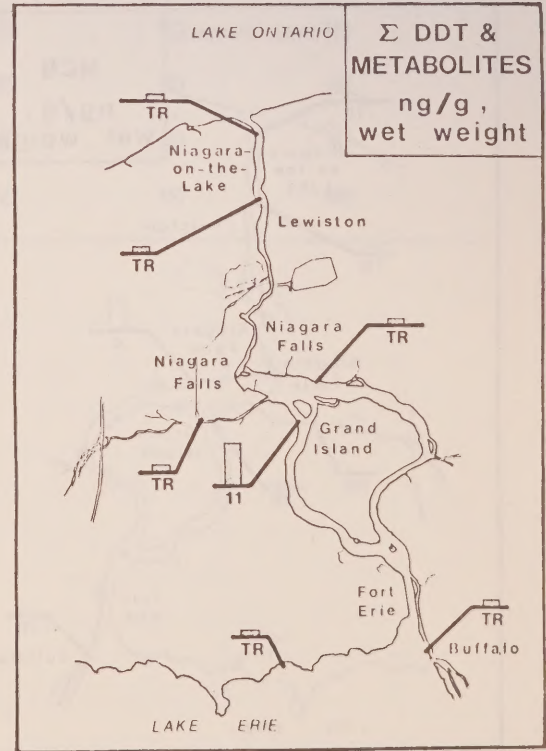
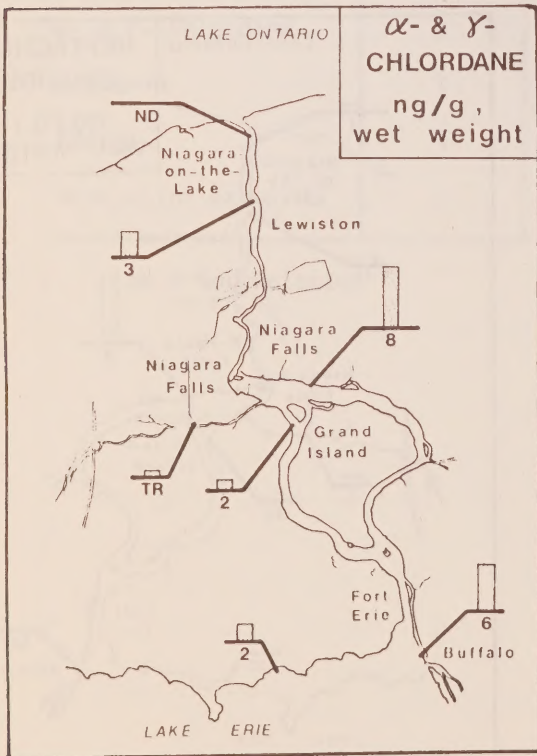
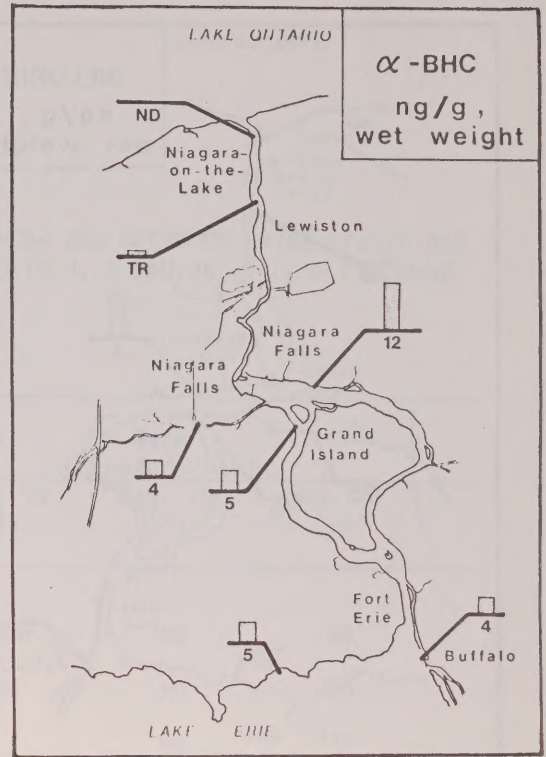
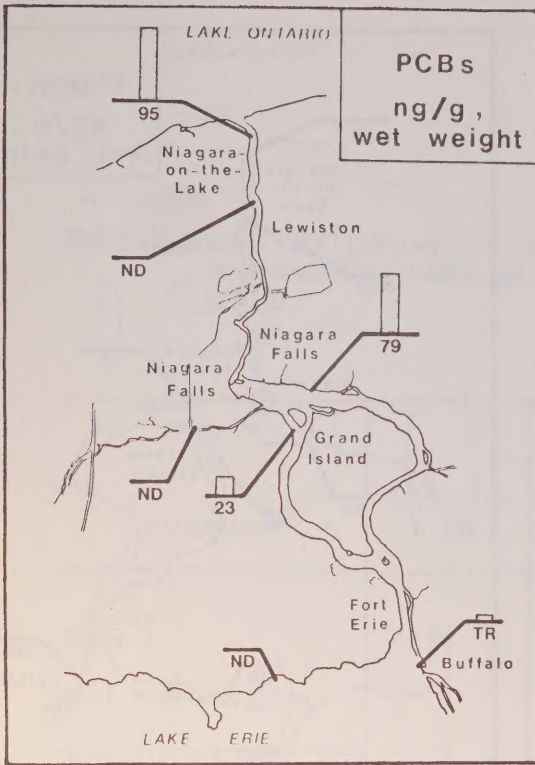


FIGURE 3. MEAN CONCENTRATIONS OF PCBs, Σ DDT + METABOLITES, DIELDRIN, ENDRIN, HCB, α -BHC, CHLORDANE AND HEPTACHLOR EPOXIDE (ng/g = ppb, wet weight) IN FRESH-WATER CLAMS (*Elliptio complanatus*) AFTER 16 DAYS' EXPOSURE TO NIAGARA RIVER WATER AT VARIOUS LOCATIONS. Values are mean of three whole clam soft tissue analyses. TR = Trace. ND = Not detected. (Cont'd.)

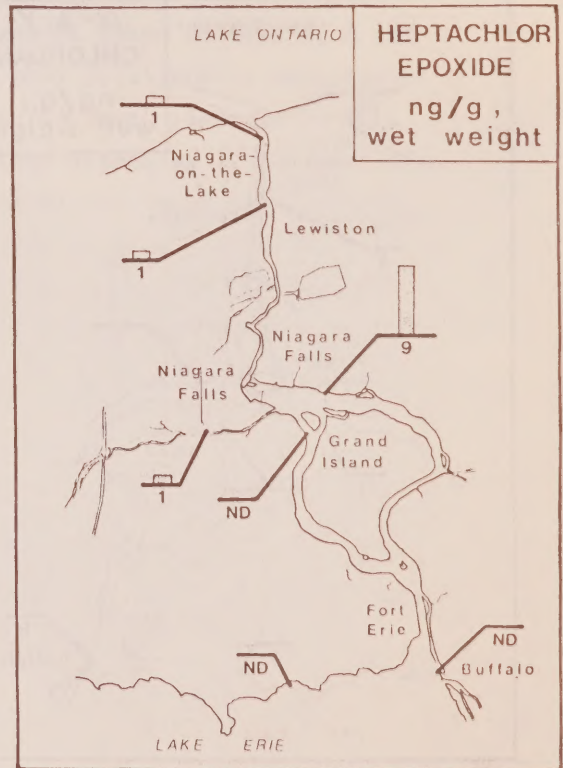
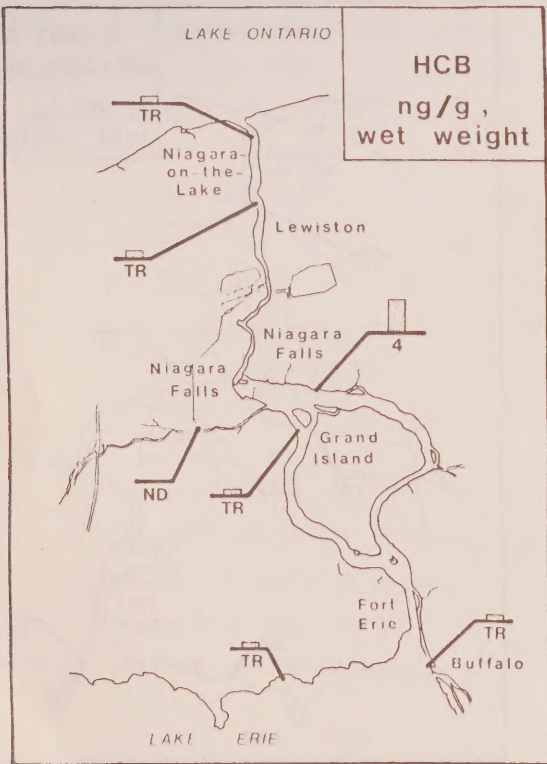
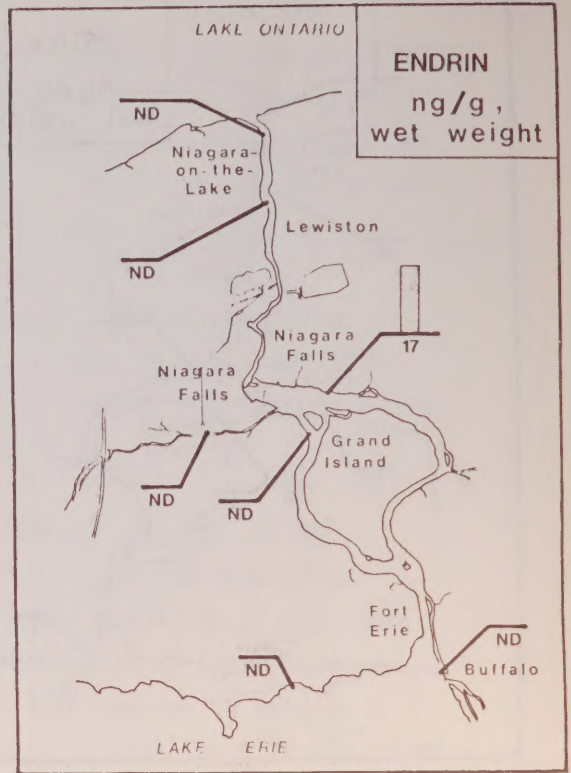
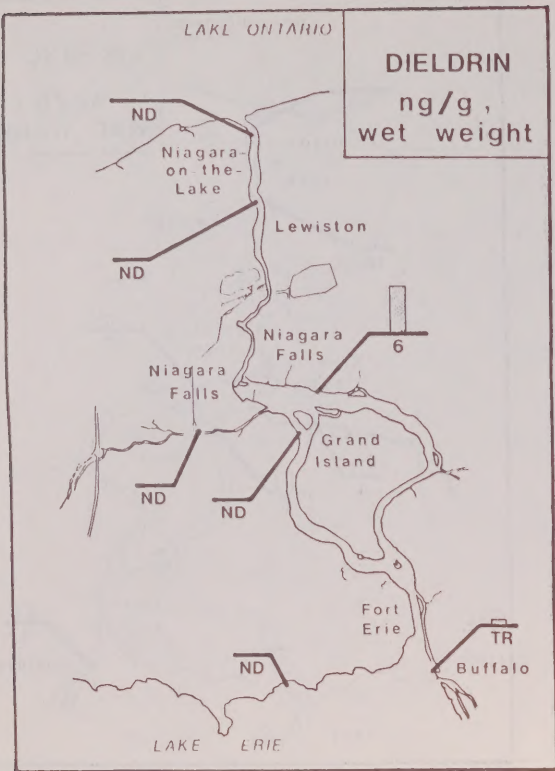


FIGURE 3. Cont'd.

TABLE 1. CONCENTRATION (ng/L = ppt) OF PCBs AND ORGANOCHLORINE PESTICIDES IN TONAWANDA CHANNEL WATER ON DAYS 4, 8 AND 16 OF CLAM EXPOSURE PERIOD.

Parameter	Detection Limit	Date (Exposure Day)		
		Aug. 16 (4)	Aug. 20 (8)	Aug. 28 (16)
PCBs	20	ND	ND	ND
ΣDDT + metabolites	5	ND	ND	ND
Hexachlorobenzene	1	1	ND	1
α-BHC	1	ND	ND	20
α- & γ- Chlordane	1	ND	ND	ND
Dieldrin	1	ND	ND	ND
Endrin	1	ND	ND	ND
Heptachlor expoxide	1	ND	ND	ND

ND = Not detected

from the Chippawa Channel, at 23 ppb, were near the detection limit (20 ppb) for this class of compound. The highest concentrations of total DDT plus metabolites (11 ppb) were detected in clams at this location, whereas only trace concentrations (<5 ppb) were found in clams from other locations in the river as well as Thunder Bay. This DDT was composed of the DDT metabolites p,p-DDE and p,p-DDD; no fresh DDT was found in clam tissues. The lack of any known sources of these two classes of compound in this channel suggests upstream influences.

Clams located in the Welland River and the lower Niagara River at Queenston and Niagara-on-the-Lake contained levels of total DDT plus metabolites, dieldrin, endrin, hexachlorobenzene and heptachlor epoxide very similar to those in the background control clams from Thunder Bay, Lake Erie.

Clams from Balsam Lake contained detectable concentrations of α -BHC (8 ppb), γ -BHC (2 ppb), γ -chlordane (21 ppb), p,p-DDE (4 ppb) and hexachlorobenzene (3 ppb); PCBs and the other organochlorine pesticides were not detected in their tissues. However, the above organochlorine pesticide residues were quickly lost (within 2 to 4 days) by clams situated in sites not exposed to continuous inputs of these compounds (e.g. α -BHC in clams at the Niagara-on-the-Lake vs. Tonawanda Channel site - see Figure 4).

For exposure periods from 1 to 16 days, water temperature was approximately constant ($23.4 \pm 0.7^{\circ}\text{C}$) at all stations. However, clams were also exposed for longer periods (32, 64 and 101 days). During this time, mean river water temperature dropped from 23.4°C on day 16 (August 28) to 4.5°C on day 101 (November 21). Water temperature appeared to have a significant effect on PCBs content of clams. For example, mean PCBs content in clams from the Tonawanda Channel site dropped almost 40% from 79 ppb on August 28 to 50 ppb on November 21. This may be related to a decreased filtration rate of clams at the lower temperature (Walne, 1972), and hence, a decreased uptake of contaminants. However, other factors, such as the variable nature of loadings of contaminants such as PCBs to the river (Canada-Ontario Review Board, 1980) may also contribute to

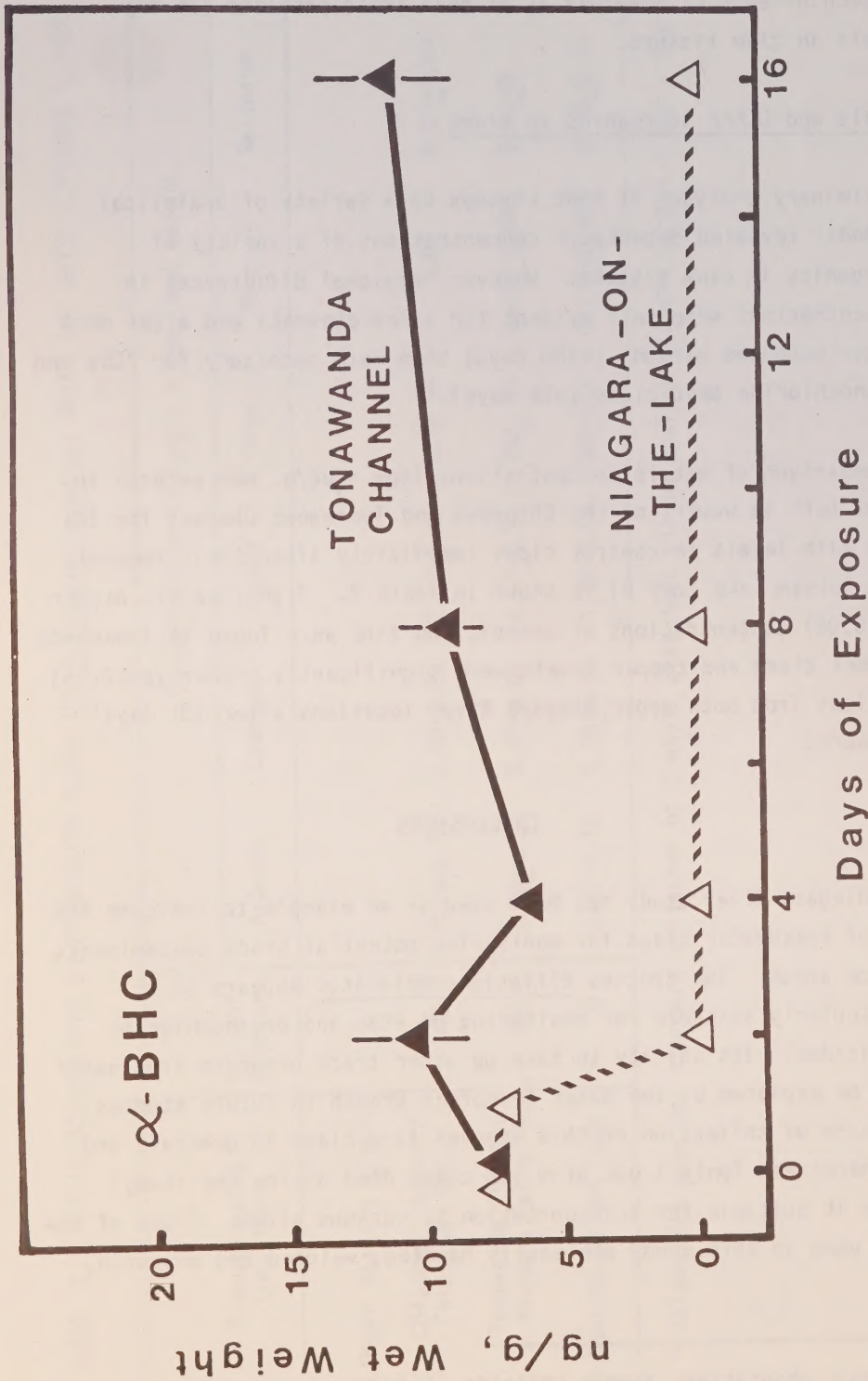


FIGURE 4. EFFECT OF EXPOSURE TIME ON α -BHC CONCENTRATION IN FRESHWATER CLAMS (*Elliptio complanatus*) PLACED IN THE NIAGARA RIVER (Aug. 12 - Aug. 28/80). Values (ng/g = ppb, wet weight) are mean and standard deviation of three whole clam soft tissue analyses. Detection limit = 1 ng/g.

this decline, particularly since concentrations of organochlorine pesticides such as α -BHC, chlordane, hexachlorobenzene and heptachlor epoxide remained at or near their previous (16 day) levels in clam tissues.

Metals and Other Inorganics in Clams

Preliminary analyses of soft tissues by a variety of analytical methods* revealed detectable concentrations of a variety of inorganics in clam tissues. However, regional differences in concentrations were only evident for a few elements and after much longer exposure periods (~ 100 days) than were necessary for PCBs and organochlorine pesticides (~ 16 days).

A comparison of metals concentrations (ppm = $\mu\text{g/g}$, wet weight) in clams left in waters of the Chippawa and Tonawanda Channel for 101 days with levels in control clams immediately after their removal from Balsam Lake (day 0) is shown in Table 2. Significantly higher ($p < 0.05$) concentrations of arsenic and zinc were found in Tonawanda Channel clams and copper levels were significantly higher ($p < 0.05$) in clams from both upper Niagara River locations after 101 days' exposure.

CONCLUSIONS

The Niagara River study has been used as an example to indicate the use of freshwater clams for monitoring potential trace contaminants source areas. The species Elliptio complanatus appears to be particularly suitable for monitoring of PCBs and organochlorine pesticides. Its ability to take up other trace organics from water will be explored by the Water Resources Branch in future studies. The ease of collection of this species (and clams in general) and its hardiness (only 1 out of ~ 500 clams died during the study) makes it suitable for transportation to various sites. Clams of the size used in this study are easily handled, weighed and measured,

* atomic absorption, atomic emission, inductively-coupled plasma, x-ray fluorescence and D.C. arc.

TABLE 2. METALS ACCUMULATED BY FRESHWATER CLAMS (Elliptio complanatus) AFTER 101 DAYS' EXPOSURE - 1980.

Biomonitoring Location	Days of Exposure	Concentration* in $\mu\text{g/g}$ = ppm, wet weight.						
		Arsenic	Cadmium	Copper	Iron	Mercury	Selenium	Zinc
Upper Niagara River:								
Chippawa Channel/ Chippawa, Ont.	101	0.89+0.29	0.90+0.26	2.87+0.31	325+ 96	0.01	0.57+0.06	30.3+2.5
Tonawanda Channel/ Niagara Falls, N.Y.	101	1.30+0.10	0.97+0.06	4.53+0.21	302+ 39	0.018+0.013	0.60+0	54.7+0.6
Control/Balsam Lake	0	0.67+0.12	0.70+0.10	1.56+0.06	380+204	0.036+0.020	0.60+0.20	35.7+4.6

* Values are mean and standard deviation of 3 whole clam soft tissue analyses (shell length = 6.5 - 7.2 cm).

and a single clam provides sufficient material for most types of laboratory analyses. Since clams are contained in easily-handled cages, they may be placed on the bottom or suspended in the water column, depending on the requirements at a particular location. Unlike native clams, introduced clams in cages enable one to determine the relative magnitudes of inputs in a given area over a predetermined time period. Also, because of their filter-feeding habit, there is no need for regular feeding by the investigator, as is usually the case with caged fish studies.

Vandalism of cages at one location did occur, with the attendant loss of most of the data. This problem can be overcome to varying degrees by better siting (away from populated or highly-frequented areas, if possible) and the use of submerged markers. Since the filtration rate of clams can be related to temperature and current speed (Walne, 1972) this can influence their exposure to trace contaminants and may result in relatively high variability between samples exposed at locations with widely-divergent physical characteristics. The use of background control stations is therefore advisable.

Depending on the magnitude of the source area, freshwater clams of the species Elliptio complanatus can accumulate detectable levels of PCBs and some organochlorine pesticides after only two days' exposure. However, to obtain maximum concentrations, an exposure period of 8 to 16 days is preferable. In areas with highly variable loading, it may be advisable to conduct repeated exposures, each time using a fresh set of clams. If this species is to be used for biomonitoring of heavy metals and other inorganics, long exposure times on the order of 3 months are necessary.

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RESEARCH NEEDS OF THE
MINISTRY OF THE ENVIRONMENT

Produced by

THE RESEARCH ADVISORY COMMITTEE

November 1981

RESEARCH NEEDS

The Research Advisory Committee administers the Provincial Lottery Funds dedicated for the use of this Ministry. In order to properly meet this challenge, it is necessary to identify and prioritize the Research Needs. The committee has tried several methods in the past, none of which came up to our expectations. Our latest effort has been moderately successful and we would like to share the method and the results with you today.

The purpose of the exercise was to generate a list of priority research needs in each of a number of predefined areas. In this regard, it was considered that the existing Acid Rain Program provided adequate resources towards that topic. The classifications developed are shown in TABLE 1. The research needs developed in the previous unsuccessful efforts were then allocated to their respective classifications.

The committee then arranged to bring together at the Resources Road complex, staff from our Regions and our Head Office group who would be capable of presenting, reviewing and prioritizing the research needs. The staff were first divided into groups of common interest, i.e. Pollution Control, Water Resources, Air Resources, Waste Management and Analytical Methods. Only four groups are illustrated on TABLE 2 and asked to review the list and remove any needs that should not be included and to add any appropriate new research needs and identify those priority needs which were being adequately addressed at present.

The new lists were prepared overnight and the following morning the groups were restructured so that each discipline was represented in every group as shown on TABLE 2. The identified needs

were assigned, with each group having about one quarter of the list to review. The needs were first evaluated high, medium or low with no more than half to be in the high group and the high group were to be prioritized. The four groups then met as a committee of the whole and presented their results for challenge and the attached tables summarise the results.

TABLE 3 and 4 summarise the research needs which are being adequately addressed at the present time.

TABLE 5, 6, 7, 8 and 9 list the highest research needs identified in each category in order of their priority.

TABLE 1

<u>Classification A:</u>	Isolation, Identification and Quantification of Contaminants and Hazardous Contaminants and their Environmental Effects.
<u>Classification B:</u>	Human Health Effects and the Development of Methods of Risk Assessment.
<u>Classification C:</u>	Management Treatment and Containment of Wastes and Hazardous Substances.
<u>Classification D:</u>	Management and Treatment of Drinking Water, Wastewater and Urban Run-off.
<u>Classification E:</u>	Transportation, Deposition and Interaction of Pollutants Throughout the Ambient Environment and Environmental Management.

TABLE 2

IDENTIFICATION OF RESEARCH NEEDS

1	1	2	2	3	3	4	4
1	1	2	2	3	3	4	4

EVALUATION AND PRIORITY SETTING

1	3	1	3	1	3	1	3
2	4	2	4	2	4	2	4

TABLE 3

SUBJECTS FROM GROUPS A, B & C CONSIDERED
TO BE ADEQUATELY ADDRESSED

- Group A: Identification of hazardous substances produced during treatment of drinking water;
- (a) by chlorination;
 - (b) by ozonation;
 - (c) by other chemicals.
- Identification of constituents (at least 80%) of total suspended particulates from hi-vol filters.
- Group B: Continue work on developing a universal transportation noise descriptor.
- Investigate methods for setting noise standards for replacement parts of vehicles, i.e. mufflers.
- Develop standard procedures for setting acceptable community noise limits for legal purposes.
- Group C: To minimize sludge disposal problems while utilizing the values inherent in sludge composition.
- Investigate patterns of gas production and migration from landfill sites.
- Develop criteria for siting structures on and adjacent to landfill sites and how such structures are affected by the site.

TABLE 4

SUBJECTS FROM GROUPS D & E CONSIDERED
TO BE ADEQUATELY ADDRESSED

Group D: Investigation of the use of natural systems,
(i.e. marshes, swamps), for treatment of wastes.

Optimum solid loadings in clarifier and increase
process efficiency by reducing flow-through time.

Group E: Better definition of the linkage between ambient
water quality criteria and effluent requirements.

Modelling of dissolved oxygen depletion rates
and acidification in stratified lakes relative
to nutrient and contamination inputs.

Evaluation of effects of thermal pollution on
the microbial populations and their activities
in impacted waters.

A study of the cycling of metals through vegetation,
especially on revegetated tailings or waste
disposal areas.

TABLE 5

A. Isolation, Identification and Quantification of Contaminants and Hazardous Contaminants and their Environmental Effects

1. Effects of hazardous contaminants on the aquatic environment and determination of safe ambient levels (for biota as well as human health).
2. Development of devices and procedures for "concentrated" samples to provide greater accuracy for ambient air and water contaminant analyses, especially in regard to hazardous contaminants.
3. Development of methods for emergency sampling of air pollution. Should include on-site fast quantitative tests.
4. Continued development of analytical methods for environmental contaminants.

TABLE 6

B. Human Health Effects and the Development of Risk Assessment

1. The impact on human health of exposure to hazardous airborne (inhalation) and waterborne (ingestion) contaminants and determination of safe levels.
2. Develop alternative methods to define risk of hazardous substances to humans.
3. Develop rapid and simple test strategies for detection and evaluation of mutagenic, teratogenic and carcinogenic hazards including, pure compounds, mixtures and environmental samples.
4. Epidemiological studies to evaluate the impact of specific industries on human health. (This need is partly included in B2 above).

TABLE 7

C. Management, Treatment and Containment of Wastes and Hazardous Substances

1. Examination of the safety and feasibility of the land application of sewage sludge from a virological standpoint and viewpoint of adverse health effects.
2. Effectiveness of leachate collection systems at landfill sites.
3. Determination of infiltration rate through land covers.
4. Development of demonstration or models of non-point pollution remedial measures.
5. Development of technical information for digested sludge disposal application in non-agricultural areas.
6. Improve methods for treatment and disposal of liquid industrial wastes.

TABLE 8

D. Management and Treatment of Drinking Water, Wastewater and Urban Run-off

1. Development of treatment methods for the removal of hazardous material from industrial and municipal wastewaters and sludges using existing facilities and secondly, using alternate add-ons.
2. Development of treatment methods for the removal of hazardous materials found in raw water or created during treatment using first existing water treatment systems and secondly, using alternate or add-on systems.
3. Identification of industrial materials not removed in municipal wastewater treatment plants and development of guidelines for industrial discharges and pretreatment processes.
4. Evaluation of efficiency of treatment methods for the removal or inactivation of viruses present in raw water.
5. Identification and quantification of toxic or hazardous substances from urban-runoff and development of treatment methods.
6. Examination of the efficiency of sewage treatment plant operations and disinfection alternatives with respect to the removal and inactivation of viruses.
7. Look for more cost effective methods of obtaining high quality effluents from waste treatment plants.
8. Cost effective treatment systems for private well water contaminated with bacteria, nitrates, chlorides, etc.
9. Look for more cost effective methods of obtaining high quality drinking water from water treatment plants.

E. Transportation, Deposition and Interaction of Pollutants
Throughout the Ambient Environment and Environmental Management

1. Develop practical methods to reclaim acidified lakes or to buffer lakes to prevent further acidification.
2. Effects on soil and vegetation:
 - (a) dose response criteria and thresholds;
 - (b) effects of long-term variable levels;
 - (c) acid precipitation effect on soil and vegetation.
3. A study of the cause and effect on aquatic systems of high aluminum concentrations in acidified lakes.
4. Dry deposition during air transport of pollutants.
5. Precipitation scavenging during air transport of pollutants.
6. Study more systematically the economic social benefits and costs of environmental protection programs and pollution control activities.
7. Investigate the persistence of contaminants in groundwater and in various hydrogeologic flow systems.
8. The characteristics of transport and the degradation of PCB material in soils.
9. Field concentration of heavy metals and organics in water.
10. Establish relationships of different phosphorus species to aquatic plant and algae production.
11. Kinetics and mechanisms of formation of secondary pollutants in air, water and land.
12. Development of the techniques of "in-stream management" as a viable option as the cost/benefit of waste treatment deteriorates.
13. Inline stack continuous monitoring and analysing of air for selected parameters.
14. Interfacing a graphite furnace atomizer to flame AAS or ICP-AES for direct solid sampling of powdered samples.
15. Development of atomic fluorescence methods for the determination of trace amounts of metals in atmospheric and other low-level substrates.

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